CALCULATION OF THE VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF LIQUIDS AND SOLIDS, ESPECIALLY BELOW ONE ATMOSPHERE

by

W. T. ZIEGLER

[and others]

Project A-663

Engineering Experiment Station
Georgia Institute of Technology
Atlanta, 1963

CONTENTS

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

January 7, 1963

Progress Letter No. 1

TO: Mr. B. W. Birmingham, Scientific Officer

FROM: W. T. Ziegler, Project Director

SUBJECT: Progress on Contract No. CST 7404 for the period December 1, 1962 through December 31, 1962.

1. Calculation of the vapor pressure of nitrogen below 1 atm. pressure.

The literature survey of pertinent data has been brought up to date. Calculations of the vapor pressure and heats of vaporization and sublimation have been completed to 20° K for two somewhat different expressions for the second virial coefficient computed (a) using a Lennard-Jones (6-12) potential function fitted by least squares procedure to existing second virial coefficient data; (b) using the Kihara core model with constants taken from paper by Prausnitz and Myers (presented at Denver meeting AIChE, August, 1962). It is expected that computations on nitrogen will be completed and rough draft of technical report summarizing results will be begun in January, 1963.

2. Calculation of the vapor pressure of fluorine below 1 atm. pressure.

A literature survey has been made to assemble the necessary thermodynamic and physical data to permit the calculation of vapor pressure of flourine as a function of temperature to about 15° K. It is hoped that computation for flourine can be completed in January.

3. Personnel associated with the project are:

J. C. Mullins, D. W. Yarbrough, and W. T. Ziegler (project director).

W. T. Ziegler
R gents Professor
Chemical Engineering

WTZ:dd

cc: B. F. Betts
B. W. Birmingham
F. Bellinger

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

February 5, 1963

Progress Letter No. 2

TO: Mr. B. W. Birmingham, Scientific Officer

FROM: W. T. Ziegler, Project Director

SUBJECT: Progress on Contract No. CST 7404 for the period January 1, 1963 through January 31, 1963

1. Calculation of the vapor pressure of nitrogen below 1 atm. pressure.

Calculations of the vapor pressure and heat of vaporization and sublimation of nitrogen from the normal boiling point to 10^{o} K have been completed using methods described earlier. A rough draft of a report summarizing the calculations and comparing them with available experimental data is approximately one-half completed.

2. Calculation of the vapor pressure of fluorine below 1 atm. pressure.

C lculations of the vapor pressure and heats of vaporization and sublimation of fluorine from the normal boiling point to 14^{o} K have been completed using the same methods as for nitrogen. The calculations have been compared with the limited data available for this substance.

3. Further work.

Technical reports covering the calculations for nitrogen and fluorine will be prepared during February, 1963. Also literature searches will be started on carbon dioxide to permit similar calculations to be made for this substance.

4. Personnel.

Personnel associated with the project during this month were J. C. Mullins, D. W. Yarbrough, and W. T. Ziegler (Project Director).

W. T. Ziegler
Regents' Professor
Chemical Engineering

WTZ:dd

cc: B. F. Betts
B. W. Birmingham
F. Bellinger

REVIEW
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FORMAT ✓ 19 BY

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

March 12, 1963

Progress Letter No. 3

TO: Mr. B. W. Birmingham, Scientific Officer

FROM: W. T. Ziegler, Project Director

SUBJECT: Progress on Contract No. CST 7404 (our Project A-663) for the Period February 1, 1963 through February 28, 1963

1. Calculation of the vapor pressure and heats of vaporization and sublimation of nitrogen and fluorine below one atmosphere pressure.

Calculations of these physical properties for nitrogen and fluorine from the normal boiling point to about 10° K have now been completed. A rough draft of a report summarizing these results has been completed during the past month.

2. Further work.

Work on the preparation of a technical report on nitrogen and fluorine to be submitted to the Cryogenic Engineering Laboratory, National Bureau of Standards, will be continued. Detailed literature searches will be begun on carbon dioxide and carbon monoxide to assemble the necessary information to permit similar calculations to be made for these substances. Some of this material has already been assembled.

3. Personnel.

Personnel associated with the project during this month were J. C. Mullins and W. T. Ziegler (Project Director).

W. T.

W. T. Ziegler
Regents' Professor
Chemical Engineering

WTZ:dg

cc: B. F. Betts
B. W. Birmingham
F. Dellinger

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

April 11, 1963

Progress Letter No. 4

TO: Mr. B. W. Birmingham, Scientific Officer

FROM: W. T. Ziegler, Project Director

SUBJECT: Progress on Contract No. CST-7404 (our Project A-663) for the Period 1 March through 31 March, 1963.

1. Calculation of the vapor pressure and heats of vaporization and sublimation of nitrogen and fluorine below one atmosphere pressure.

Calculations of these physical properties for nitrogen and fluorine from the normal boiling point to about 10^{0} K were completed during February, 1963. The rough draft of the report describing these calculations which was completed during February has been revised and is now in final form suitable for reproduction.

2. Calculation of the vapor pressure and heats of sublimation of carbon dioxide below one atmosphere pressure.

A literature search to assemble the information necessary for making these calculations is in progress.

3. Further work.

Work on the preparation of a technical report on nitrogen and fluorine to be submitted to the Cryogenic Engineering Laboratory, National Bureau of Standards, will be continued. Detailed literature search on carbon dioxide will be continued. A similar literature search for data on carbon monoxide will be begun if time and personnel permits.

4. Personnel.

Personnel associated with the project during this month were J. C. Mullins and W. T. Ziegler (Project Director).

W. T. Ziegler
Regents' Professor
Chemical Engineering

WTZ:dg

cc: B. F. Betts
B. W. Birmingham
F. Bellinger
M. W. Bennett

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

May 6, 1963

Progress Letter No. 5

TO: Mr. B. W. Birmingham, Scientific Officer

FROM: W. T. Ziegler, Project Director

SUBJECT: Progress on Contract No. CST-7404 (our Project A-663) for the Period 1 April through 30 April, 1963.

1. Calculation of the vapor pressure and heats of vaporization and sublimation of nitrogen and fluorine below one atmosphere pressure.

Final typing of a report covering calculations of these properties for nitrogen and fluorine from the normal boiling point to about 10^{0} K has been started. Preparation of figures for reproduction is in progress. It is hoped that this report can be issued by June 15.

2. Calculation of the vapor pressure and heats of sublimation of carbon dioxide below one atmosphere pressure.

A literature search to assemble the information necessary for making these calculations is in progress.

3. Calculation of the vapor pressure and heats of vaporization and sublimation of carbon monoxide.

A literature search to assemble the information necessary for making these calculations is in progress.

4. Further work.

Literature searches covering the necessary information for carbon dioxide and carbon monoxide will be continued. Analysis of the data will be carried out and calculations will be started as soon as feasible.

5. Personnel.

Personnel associated with the project during this month were J. C. Mullins and W. T. Ziegler (Project Director). Mr. B. S. Kirk began working with the project during the last week of April and will continue to do so until August 31.

WTZ:dg

W. T. Ziegler
Regents' Professor
Chemical Engineering

cc: B. F. Botts
B. W. Birmingham
F. Bellinger
M. W. Bennett

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

June 5, 1963

Progress Letter No. 6

TO: Mr. B. W. Birmingham, Scientific Officer

FROM: W. T. Ziegler, Project Director

SUBJECT: Progress on Contract No. CST-7404 (our Project A-663) for the Period 1 May through 31 May, 1963.

1. Calculation of the vapor pressure and heats of vaporization and sublimation of nitrogen and fluorine below one atmosphere pressure.

A technical report covering calculations of these properties for nitrogen and fluorine from the normal boiling point to 10° K and 14° K, respectively, has been completed and will be available for distribution on about June 10.

2. Calculation of the vapor pressure and heats of sublimation of carbon dioxide below one atmosphere pressure.

A literature search to assemble the information necessary for making these calculations is essentially complete. Analysis of the collected data has been started and certain preliminary calculations made.

3. Calculation of the vapor pressure and heats of vaporization and sublimation of carbon monoxide.

A literature search to assemble the information necessary for making these calculations is essentially complete. Analysis of the collected data has been started and certain preliminary calculations made.

4. Further work.

The literature searches now underway on carbon dioxide and carbon monoxide will be completed. Calculations of the vapor pressures and heats of vaporization and sublimation of these substances will be continued. Literature searches designed to collect the necessary data for making similar calculations for krypton and xenon will be started. The possibility of making similar calculations for "normal" hydrogen will be considered.

5. Personnel

Personnel associated with the project on a part-time basis during this month were J. C. Mullins, B. S. Kirk, and W. T. Ziegler (Project Director). Mr. D. W. Yarbrough, graduate student in Chemical Engineering, will begin work with the project on about June 10.

W. T. Ziegler
Regents' Professor
Chemical Engineering

WTZ;dg

cc: B. F. Betts
B. W. Birmingham

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

July 1, 1963

Progress Letter No. 7

TO: Mr. B. W. Birmingham, Scientific Officer

FROM: W. T. Ziegler, Project Director

SUBJECT: Progress on Contract No. CST-7404 (our Project A-663) for the Period 1 June through 30 June, 1963.

1. Calculation of the vapor pressure and heats of vaporization and sublimation of nitrogen and fluorine below one atmosphere pressure.

A technical report: Technical Report No. 1, Calculation of the Vapor Pressure and Heats of Vaporization and Sublimation of Liquids and Solids, Especially Below One Atmosphere. IV. Nitrogen and Fluorine. W. T. Ziegler and J. C. Mullins (National Bureau of Standards Contract No. CST-7404) dated April 15, 1963, was sent to the contractor early in June. Three hundred copies of this report were sent to Mr. V. J. Johnson, CEL-NBS, under NBS Purchase Order No. 28031-3.

On June 28, a small computational error was discovered in the vapor pressure tables for nitrogen and fluorine, as well as the tables issued earlier for argon (Tech. Rpt. No. 2, Calculation of Vapor Pressure and Heats of Vaporization and Sublimation of Liquids and Solids, Especially Below One Atmosphere. II. Argon. W. T. Ziegler, J. C. Mullins and B. S. Kirk (NBS Contract No. CST-7238) dated June 15, 1962)). Errata sheets covering these reports will be issued by July 15. No such errors are present in earlier reports dealing with parahydrogen, oxygen, ethylene and methane.

2. Calculation of the vapor pressure and heats of sublimation of carbon dioxide below one atmosphere pressure.

A literature survey to assemble the information necessary for making these calculations has been completed. Analysis of the collected data is nearing completion.

3. Calculation of the vapor pressure and heats of vaporization and sublimation of carbon monoxide.

A literature survey to assemble the information necessary for making these calculations has been completed. Analysis of the collected data is nearing completion.

4. Calculation of the vapor pressure and heats of vaporization and sublimation of normal hydrogen, krypton and xenon.

A literature search to assemble the information necessary for making these calculations for normal hydrogen and krypton is nearing completion. Some information has also been collected for xenon.

5. Further work.

The preparation of a technical report covering the calculations for carbon dioxide and carbon monoxide will be undertaken. The literature search for information necessary for making similar calculations for normal hydrogen and krypton will be completed. Analysis of the collected data and calculations based upon them will be started.

6. Personnel.

Personnel associated with the project on a part-time basis during this month were J. C. Mullins, B. S. Kirk, D. W. Yarbrough and W. T. Ziegler (Project Director).

W. T. Ziegler
Regents' Professor
Chemical Engineering

WTZ:lg
cc: B. F. Betts (2)

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

August 2, 1963

Via Air Mail

National Bureau of Standards
Boulder, Colorado

Attention: Mr. Barton F. Betts
Contracting Officer

Dear Mr. Betts:

I enclose herewith two copies of Progress Letter No. 8 reporting the progress on Contract No. CST-7404 (our Project A-663) for the period 1 July through 31 July, 1963. It is my understanding that this report will be transmitted to Mr. B. W. Birmingham through your office.

Very truly yours,

J. C. Mullins

JCM:js

Enclosures

bcc: F. Bellinger
Library (2)

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

August 2, 1963

Progress Letter No. 8

TO: Mr. B. W. Birmingham, Scientific Officer

FROM: W. T. Ziegler, Project Director

SUBJECT: Progress on Contract No. CST-7404 (our Project A-663) for the Period 1 July through 31 July, 1963.

1. Calculation of the vapor pressure and heats of vaporization and sublimation of carbon monoxide and carbon dioxide below one atmosphere pressure.

The analysis of the data has been completed as well as a rough draft of the technical report.

2. Calculation of the vapor pressure and heats of vaporization and sublimation of krypton.

A literature survey to assemble the data necessary for making these calculations has been completed. Some preliminary calculations have been made.

3. Calculation of the vapor pressure and heats of vaporization and sublimation of normal hydrogen and xenon.

A literature survey to assemble the information necessary to make the calculations for normal hydrogen has been completed. No further work has been done on xenon.

4. Further work

The technical report on the calculations for carbon monoxide and carbon dioxide will be completed. Calculations on krypton and normal hydrogen will be continued.

5. Personnel

Personnel associated with the project on a part time basis during this month were J. C. Mullins, B. S. Kirk, D. W. Yarbrough and W. T. Ziegler (Project Director).

J. C. Mullins
for W. T. Ziegler
Project Director

JCM:js
cc: B. F. Betts (2)

TECHNICAL REPORT NO. 1

PROJECT NO. A-663

CALCULATION OF THE VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF LIQUIDS AND SOLIDS, ESPECIALLY BELOW ONE ATMOSPHERE. IV. NITROGEN AND FLUORINE.

W. T. ZIEGLER AND J. C. MULLINS

Contract No. CST-7404
National Bureau of Standards
Boulder, Colorado

April 15, 1963

Engineering Experiment Station
GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia

CORRECTIONS
TO
REPORT ENTITLED

"Calculation of the Vapor Pressure and Heats of Vaporization and Sublimation o Liquids and Solids, Especially Below One Atmosphere. IV. Nitrogen and Fluori

W. T. Ziegler and J. C. Mullins. Engineering Experiment Station, Georgia Institute of Technology. Technical Report No. 1, April 15, 1963, to Cryogenic Engineering Laboratory, National Bureau of Standards, Boulder, Colorado, under NBS Contract CST-7404.

- -

A small error has been discovered in the computational procedure used to compute the vapor pressure and heats of vaporization and sublimation of both nitrogen and fluorine presented in the above mentioned report. This error necessitates a small correction of Table XVI for nitrogen and Table XVII for fluorine and the replotting of a few points in Figures 3 and 7. The error does not affect any of the conclusions reached in the report. Several typographical errors which have been found are also listed.

NITROGEN

The values given in Table XVI, page 56, should be replaced by the correct values given below.

Temperature, T (°K)	Pressure, P (mm Hg)	Heat of Vaporization (cal/gm mole)	$(1/T) \times 10^2$ ($°K^{-1}$)	Log P
56	17.736	1645.3	1.78571	1.248861
55	13.544	1648.9	1.81818	1.131745
54	10.235	1652.4	1.85185	1.010080
53	7.649	1655.8	1.88679	0.883590
52	5.650	1659.1	1.92307	0.752034
51	4.122	1662.2	1.96078	0.615057
50	2.968	1665.3	2.00000	0.472390
49	2.107	1668.3	2.04081	0.323628
48	1.474	1671.1	2.08333	0.168442
47	1.015	1673.9	2.12765	0.006368
46	6.871 (-1)	1676.6	2.17391	-0.162991
45	4.569 (-1)	1679.2	2.22222	-0.340164
44	2.981 (-1)	1681.7	2.27272	-0.525667
43	1.905 (-1)	1684.1	2.32558	-0.720060
42	1.191 (-1)	1686.4	2.38095	-0.924002
41	7.275 (-2)	1688.6	2.43902	-1.138167

The following data points plotted in Figure 3, page 19, should be correcte
All other points in the affected temperature range are changed by less than
0.002° K.

Temperature (°K)	$T_{calc} - T_{obs}$ (°K) Plotted	Corrected	Observer
55.86	-0.0146	-0.0228	Giauque and Clayton (29)
54.78	-0.0112	-0.0174	Giauque and Clayton (29)
55.80	-0.0174	-0.0262	Keesom and Bijl (52)
53.25	-0.0151	-0.0192	Keesom and Bijl (52)

FLUORINE

The values given in Table XVII, page 58, should be replaced by the correc values given below.

Temperature, T (°K)	Pressure, P (mm Hg)	Heat of Vaporization (cal/gm mole)	$(1/T) \times 10^2$ ($°K^{-1}$)	Log P
62	18.553	1736.5	1.61290	1.268423
61	14.711	1743.4	1.63934	1.167636
60	11.564	1750.2	1.66667	1.063124
59	9.009	1757.1	1.69491	0.954684
58	6.952	1763.9	1.72413	0.842101
57	5.311	1770.8	1.75438	0.725145
56	4.014	1777.6	1.78571	0.603568
55	3.000	1784.5	1.81818	0.477105
54	2.215	1791.4	1.85185	0.345469
53.54 (t.p.)	1.919	1794.6	1.86776	0.283096
53.54 (t.p.)	1.919	1916.6	1.86776	0.283096
53	1.597	1919.4	1.88679	0.203297
52	1.124	1924.6	1.92307	0.050838
51	7.798 (-1)	1929.7	1.96078	-0.108007
50	5.326 (-1)	1934.6	2.00000	-0.273625
49	3.577 (-1)	1939.4	2.04081	-0.446427
48	2.361 (-1)	1944.0	2.08333	-0.626860
47	1.530 (-1)	1948.5	2.12765	-0.815408
46	9.714 (-2)	1952.8	2.17391	-1.012597
45.55 (tr.)	7.865 (-2)	1954.7	2.19538	-1.104300
45	5.900 (-2)	2130.6	2.22222	-1.229176
44	3.431 (-2)	2134.0	2.27272	-1.464545

The following data points plotted in Figure 7, page 36, should be correct All other points in the affected temperature region are changed by less than 0.002° K.

Temperature (°K)	$T_{calc} - T_{obs}$ (°K) Plotted	Corrected	Observer
61.93	-0.007	-0.017	Hu, White & Johnston (45
60.45	-0.043	-0.051	Hu, White & Johnston (45
58.93	-0.097	-0.102	Hu, White & Johnston (45
57.41	-0.142	-0.146	Hu, White & Johnston (45
59.45	-0.429	-0.435	Aoyama and Kanda (5)

ADDITIONAL CORRECTIONS

Page 11, line 16. Change 33.62°K to 35.62°K

Page 22, Table VII. Change Kinshenbaum to Kirshenbaum

Change Verchoyle to Verschoyle

July 2, 1963

W. T. Ziegler and J. C. Mullins

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

TECHNICAL REPORT NO. 1

PROJECT NO. A-663

CALCULATION OF THE VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF LIQUIDS AND SOLIDS, ESPECIALLY BELOW ONE ATMOSPHERE. IV. NITROGEN AND FLUORINE.

By

W. T. ZIEGLER AND J. C. MULLINS

CONTRACT NO. CST-7404
NATIONAL BUREAU OF STANDARDS
BOULDER, COLORADO

April 15, 1963

ABSTRACT

The vapor pressure and heats of vaporization and sublimation of nitrogen and fluorine have been computed at one degree intervals from the normal boiling point to 10° K and 14° K, respectively, using available thermodynamic data. The computed results have been compared with the published experimental data.

The excellent agreement obtained between the computed and experimental vapor pressure data for nitrogen in the liquid and solid range suggest that the computed values may well represent the experimental data within the accuracy of the temperature scales used by the several investigators. The computed values are therefore recommended for use as smoothed values, especially in the solid range below 50° K where the available experimental data are scattered and discordant.

For liquid fluorine the agreement between the computed values and the experimental data of Hu, White and Johnston is good except near the triple point. The limited measurements of other investigators, which appear to be less accurate than those of Hu et al., show significant disagreement with the computed values. For solid fluorine the computed values differ considerably from the single published set of limited experimental data. In view of the limited and scattered nature of the experimental data for fluorine, it is recommended that the computed vapor pressure values be used as a smoothed representation of the vapor pressure of fluorine, especially in the solid range.

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This report contains 59 pages.

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I. INTRODUCTION

In a previous report[86] a number of thermodynamic relations were presented for the calculation of the vapor pressure and heats of vaporization and sublimation of liquids and solids. These thermodynamic relations are similar in principle to relations developed by other investigators.[32,33,76,26,71] These relations have been used to compute the vapor pressures and heats of vaporization and sublimation of ethylene,[86] oxygen,[64] argon,[87] and methane,[88] from approximately the normal boiling point to 20° K and of parahydrogen[63] from 22° to 1° K.

The present report is concerned with the application of the thermodynamic relations previously developed[86] to nitrogen and fluorine. The principal thermodynamic relations used are summarized in the next section. The necessary available thermodynamic data have been used to compute the vapor pressure and heats of vaporization and sublimation of nitrogen and fluorine from their normal boiling points to 10° and 14° K, respectively. The computed results have been compared with available experimental vapor pressure and heat of vaporization data.

As in the previous reports, the temperatures reported by different investigators have been converted to the thermodynamic temperature scale with an assigned ice point of 273.15° K. On this scale the normal boiling point of oxygen has been taken to the 90.168° K. This value is based on an analysis of the various reported normal boiling points of oxygen made by van Dijk.[75] Barber[8] has recently obtained a value of 90.177 ± 0.006° K for the normal boiling point of oxygen. He has combined this value with existing data to obtain an average of 90.170° K.

The energy quantities appearing in the calculations are expressed in terms of the defined calorie (1 calorie = 4.1840 ab. joule = 4.1833 int. joules). No attempt was made, however, to correct experimental thermal data to a uniform energy unit basis.

II. THERMODYNAMIC RELATIONS

A. Variation of Heat of Vaporization and Sublimation with Temperature

By performing an enthalpy cycle between two points, (P,T) and (P_1,T_1), on the vapor pressure curve of a pure substance it can be shown[86] that the heat of vaporization or sublimation at the temperature T_1 can be computed from Equation (1).*

$$(\Delta H_v)_T = (\Delta H_v)_{T_1} + \int_T^{T_1} c_s' \, dT + \sum_T^{T_1} (\Delta H_{tr})' - \left[(H^o - H_o^o)''_{T_1} - (H^o - H_o^o)''_T \right] - RT_1 \delta_1 + RT\delta + \int_P^{P_1} v_s' \, dP \qquad (1)$$

In this equation the quantity δ is given by the relation

$$RT\delta = [H(P,T) - H^o(T)]' \qquad (2)$$

and δ_1 is the value of δ at the point (P_1, T_1). The prime (') and double prime(") symbols refer to the condensed and vapor phases, respectively. The evaluation of the right-hand side of Equation (2) requires an equation of state for the vapor. If a virial form of the equation of state is used, namely,

$$PV = RT \left(1 + \frac{B}{V}\right) \qquad (3)$$

where the second virial coefficient, B, is assumed to be a function of temperature only, then one obtains

$$\delta = \left(B - T \frac{dB}{dT}\right) / V \qquad (4)$$

---

*All symbols are defined in Appendix A.

For temperatures below the triple point, $(\Delta H_v)_T$ in Equation (1) is the heat of sublimation rather than the heat of vaporization. The evaluation of the last two terms of Equation (1) requires a value of the vapor pressure at T. If vapor pressure calculations are made by an iterative procedure, then this iterative procedure also provides the pressure necessary to compute the last two terms of Equation (1).

B. Vapor Pressure Relations

From a known point (P_1,T_1) on the vapor pressure curve, the vapor pressure at any other point (P,T) can be calculated from the previously derived relation[86]

$$\ln P = \ln P_1 - (\Delta H_v)_{T_1} (T_1 - T)/RTT_1 + \left[(H^o - H_o^o)''_{T_1} - (H^o - H_o^o)''_T\right]/RT$$

$$- \left[(S^o)''_{T_1} - (S^o)''_T\right]/R - \left(\int_T^{T_1} c_s' \, dT\right)/RT$$

$$- \left(\sum_T^{T_1} (\Delta H_{tr})'\right)/RT + \left(\int_T^{T_1} c_s' \, dT/T\right)/R$$

$$+ \left(\sum_T^{T_1} (\Delta H_{tr})'/T_{tr}\right)/R + \delta_1 (T_1 - T)/T$$

$$- \epsilon_1 + \epsilon - \left(\int_P^{P_1} v_s' \, dP\right)/RT \qquad (5)$$

where

$$\epsilon = \left[H^o(T) - H(P,T)\right]''/RT - \left[S^o(P,T) - S(P,T)\right]''/R \qquad (6)$$

and ϵ_1 is the value of ϵ at (P_1,T_1). If the virial form of the equation of state is assumed, i.e., Equation (3), then ϵ becomes

$$\epsilon = \ln (PV/RT) - 2B/V \qquad (7)$$

Equation (5), which may be considered to be an integration of the Clapeyron equation, can be solved if appropriate thermal data for the condensed phase, $(\Delta H_v)_{T_1}$, an equation of state for the real gas, and the requisite molecular structure data for the ideal gas are available. Solution of Equation (5) requires iteration since the last two terms are pressure dependent.

III. VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF NITROGEN

A. Introduction

The vapor pressure and heats of vaporization and sublimation of nitrogen were calculated from its normal boiling point (77.347° K) to 10° K using appropriate equations from the preceding section. The calculations were made for the normally occurring isotopic mixture.[35] The thermodynamic properties of the ideal gas at one atmosphere pressure were calculated assuming a rigid-rotor harmonic-oscillator approximation.

B. Review of Experimental Data for Nitrogen

1. Introduction

The calculation of vapor pressures from Equation (5) and heats of vaporization and sublimation from Equation (1) for nitrogen in the temperature range from the normal boiling point to 10° K requires the following data: $(\Delta H_v)_{T_l}$; P_l; T_l; (ΔH_{tr}); T_{tr}; and c_s' and v_s' as a function of temperature. A representation of the second virial coefficient as a function of temperature is also required. The effect of higher virial coefficients is assumed to be negligible. In addition, the appropriate molecular structure data are required to permit calculation of the thermodynamic properties of the ideal gas.

From a survey of the literature, a selection has been made of the "best" values of these thermal and related properties of nitrogen. These selected values are summarized in Table I. The selection of these data is discussed in the following sections. The available experimental data for the vapor pressure of solid and liquid nitrogen below one atmosphere have been assembled for comparison with the computed quantities. In addition the experimental values of the heat of vaporization of nitrogen at pressures below one atmosphere determined by Furukawa and McCoskey[28] are compared with the computed values.

TABLE I

SUMMARY OF SELECTED PHYSICAL PROPERTIES OF NITROGEN

Property	Selected Value	Table No.
Normal boiling point (n.b.p.) (P = 760 mm Hg)	77.347° K	II
Triple point (t.p.)	63.152° K	II
α-β Solid transition temperature	35.62° K	II
Heat of vaporization (n.b.p.)	1334.8 cal/gm mole	III
Heat of fusion (t.p.)	172.30 cal/gm mole	III
Heat of α-β transition	54.71 cal/gm mole	III
Heat capacity of saturated condensed phases	Polynomial for appropriate temperature range	IV
Mean molal volume of liquid (63.152° - 77.347° K)	33.50 ml/gm mole	
Mean molal volume of solid (35.62 - 63.152° K)	28.67 ml/gm mole	
(10.0 - 35.62° K)	27.57 ml/gm mole	
Lennard-Jones (6-12) parameters for second virial coefficients	e/k = 90.467° K b_o = 76.869 cc/gm mole	
Molecular parameters		
Moments of Inertia		VI
N^{14} - N^{14}	1.4006×10^{-39} gm-cm^2	
N^{14} - N^{15}	1.4487×10^{-39} gm-cm^2	
Fundamental frequency	2330.72 cm^{-1}	VI
Molecular weights and isotopic composition		VI
N^{14} - N^{14} (99.28%)	28.00746*	
N^{14} - N^{15} (0.72%)	29.00454*	

*Chemical mass units

The temperatures of all transition points and vapor pressure data have been corrected, wherever possible, to a thermodynamic scale with an ice point of 273.15° K. Methods of temperature correction are given in Appendix B. No temperature corrections have been applied to heat capacity, equation of state or heat of transition data since such changes are believed to be within the experimental error of the data.

2. Phase Transition Temperatures of Nitrogen

The values of the boiling point, triple point and solid transition temperatures reported by various investigators are given below in Table II along with the selected values used in this report. Only the values of the boiling point and triple point temperatures which could be directly related to gas thermometry were used. If more than one value was reported by a laboratory only the most recent value was used to determine the selected value. Other values of the boiling point which are reported in the literature are those of Heuse and Otto,[39] Aoyama and Kanda,[3] Henning and Heuse,[37] Keesom,[51] Henning,[36] and Cath.[11] Other values of the triple point are those of Mathias and Crommelin,[57] Keesom,[51] Henning,[36] and Cath.[11]

The solid transition temperature reported by Giauque and Clayton[29] was selected primarily to be consistent with the heat capacity used in the region of the transition temperature, which was that of Giauque and Clayton.[29] Other values of the solid transition temperature have been reported by Clusius,[14] Eucken,[25] and Swenson.[74]

All temperatures were converted to the thermodynamic temperature scale with an assigned ice point of 273.15° K using the various methods described in Appendix B.

TABLE II

TRANSITION TEMPERATURES OF NITROGEN

Reported Temperature	Ice Point (°K)	Corrected[a] Temperature (°K)	Year	Reference
		- Normal Boiling Point -		
77.32° K	273.10	77.334	1933	Giauque and Clayton[29]
-195.808° C	273.16	77.349	1936	Henning and Otto[38]
-195.787° C	273.144	77.359	1937	Keesom and Bijl[52]
77.364° K	90.19[b]	77.345	1954	Armstrong[6]
Selected Value		77.347		
		- Triple Point -		
63.136° K	273.10	63.148	1933	Giauque and Clayton[29]
-210.015° C	273.16	63.143	1936	Henning and Otto[38]
63.150° K	273.144	63.151	1937	Keesom and Bijl[52]
63.180° K	90.19[b]	63.165	1953	Furukawa and McCoskey[28]
Selected Value		63.152		
		- Solid Transition -		
35.61° K	273.10	35.62	1933	Giauque and Clayton[29]

[a] For method of temperature correction see Appendix B.

[b] NBS Provisional Temperature Scale.[42]

3. Heats of Vaporization, Fusion and Transition of Nitrogen

The heats of transition which were used in this work are summarized below in Table III.

Only those values of the heat of vaporization at the normal boiling point which were determined calorimetrically were considered. Many values reported in the literature were determined from vapor pressure data using the Clapeyron equation and were not considered for this reason. Other values of the heat of

TABLE III

HEATS OF TRANSITION OF NITROGEN

	Transition Cal/gm mole	Temperature (°K)	Year	Reference
Heat of vaporization	1332.9	77.32	1933	Giauque and Clayton[29]
at the n.b.p.	1336.6		1953	Furukawa and McCoskey[28]
Selected Value	1334.8			
Heat of fusion	168.7	63.1	1916	Eucken[25]
	170.95	63.08	1929	Clusius[14]
	172.3	63.14	1933	Giauque and Clayton[29]
	172.26		1959	Clusius, et al[16]
Selected Value	172.3			
Heat of α-β	53.8	35.5	1916	Eucken[25]
Solid transition	51.4	35.4	1922	Clusius[14]
	54.71	35.61	1933	Giauque and Clayton[29]
	55.62	35.61	1959	Clusius, et al[16]
Selected Value	54.71			

vaporization which are reported in the literature but which were not considered to be of high precision as those reported in Table III are those of Alt,[1] Dana,[19] Dewar,[21] Eucken,[25] Millar and Sullivan[61] and Witt.[85] In addition to the heat of vaporization at the normal boiling point, Furukawa and McCoskey[28] measured the heat of vaporization or sublimation at several temperatures down to 62° K. These values are compared in Section C-1 with the values calculated using Equation (1).

The heat of fusion of nitrogen has been determined by Eucken,[25] Giauque and Clayton,[29] Clusius,[14] and Clusius et al.[16] The later value of Clusius et al[16] agrees almost exactly with the value determined by Giauque and Clayton[29] and only these two values were considered in choosing the selected value given in Table III.

The heat of transition of the solid at 35.62° K was taken from the work of Giauque and Clayton.[29] Their value was chosen in order to give consistency at the transition point with the values of the heat capacity and the transition temperature. Other values reported are those of Eucken,[25] Clusius,[14] and Clusius et al.[16]

4. Heat Capacity of Saturated Condensed Nitrogen

(a) Solid Nitrogen

In the solid region the heat capacity of nitrogen has been determined by Giauque and Clayton[29] (15.82° - 61.41° K), Clusius[14] (10.42° - 61.0° K), Clusius et al[16] (11.42° - 59.10° K), Eucken[25] (16.5° - 60.6° K) and by Keesom and Onnes[53] (15.27 - 61.68° K).

The heat capacity of the solid above 10° K was represented by two equations of the form

$$c_s' = A_o + A_1T + A_2T^2 + A_3T^3 + A_4T^4 \qquad (8)$$

where the coefficients were determined by the method of least squares. From 10° K to the solid transition (33.62° K) the coefficients were determined utilizing the data of Clusius[14] and Giauque and Clayton.[29] From the solid transition to the triple point the data of Giauque and Clayton[29] were used to obtain the coefficients. The coefficients are given in Table IV. Below 10° K the solid was assumed to follow the Debye heat capacity function with five degrees of freedom. The Debye constant, θ_D, was found to be 82.3° K.

(b) Liquid Nitrogen

In the liquid range the heat capacity of nitrogen has been determined by Giauque and Clayton[29] (65.02° - 77.74° K), Clusius[14] (66.9° - 73.5° K), Clusius et al[16] (65.87° - 67.59° K), Eucken[25] (64.6° - 72.7° K), Keesom and Onnes[53] (63.95° - 76.49° K) and Wiebe and Brevoort[84] (79.17° - 116.99° K). The data of Giauque[29] were represented by a straight line using the method of least squares. The constants are given below in Table IV.

TABLE IV

COEFFICIENTS OF HEAT CAPACITY POLYNOMIALS FOR NITROGEN

Range (°K)	A_o	$A_1 \times 10^1$	$A_2 \times 10^2$	$A_3 \times 10^3$	$A_4 \times 10^5$
10.00 -35.62	3.0244108	-8.2956862	9.3116545	-3.1397762	3.8190473
35.62 -63.152	24.326576	-16.223561	5.7461088	-0.84664594	0.46237120
63.152-77.347	11.618805	0.26456813	0	0	0

5. Molal Volumes of Saturated Condensed Nitrogen

(a) Solid Nitrogen

The densities of solid nitrogen reported in the literature are given in Table V. The data were plotted and a straight line drawn through the

TABLE V

DENSITY OF SOLID NITROGEN

Temperature (°K)	Density (gm/ml)	Investigator
20.5	1.0265	Dewar[22]
62.6	0.8792	Dewar[22]
20.5	1.024	de Smedt, Keesom, and Mooy[20]
39	0.995	Ruhemann[70]
45	0.982	Vegard[79]
20	1.0265	Vegard[79]
(tp)	0.956	Simon, Ruhemann and Edwards[72]

points. Values of the molal volume were assumed constant over the temperature range of each heat capacity polynomial. In the range from 10° to 35.62° K the mean value was taken to be 27.57 ml/gm mole which corresponds to a

temperature of 25.7° K. Between 35.62° and 63.152° K the mean value was taken to be 28.67 ml/gm mole at 49.4° K.

(b) Liquid Nitrogen

The density of liquid nitrogen has been determined at saturation pressure by Baly and Donnan[7] (68.8° - 83.7° K) and by Mathias et al[58] (64.7° - 125.0° K). Recently van Itterbeek and Verbeke[78] determined the density of liquid nitrogen as a function of temperature and pressure from 65.85° to 90.60° K and presented the results in equational form. Van Itterbeek's results lie between the investigators mentioned above. The equation of van Itterbeek et al[78] was used to obtain a mean value of 33.50 ml/gm mole at 71° for use in the range 63.152° to 77.347° K. This value corresponds to the temperature of the mean pressure.

6. Second Virial Coefficient and Lennard-Jones (6-12) Parameters

The second virial coefficient of nitrogen has been determined by a number of investigators.[12,27,43,65,77,67,60] These data were used to determine the values of the Lennard-Jones (6-12) parameters, $e/k = 90.467°$ K, $b_o = 76.869$ cc/gm mole by a least squares procedure as discussed in Appendix C.

The second virial coefficient and its temperature derivative have also been calculated from the Kihara[54] core model taking into account quadrupole interactions of nitrogen molecules. The method of calculation and the necessary parameters for the Kihara core model and the quadrupole interaction are given by Prausnitz.[69] Details of this calculation are given in Appendix C.

7. Thermodynamic Functions of the Ideal Gas

The thermodynamic functions $(H^o - H_o^o)''$ and $(S^o)''$ of nitrogen in the ideal gas state at one atmosphere pressure were calculated assuming a

rigid-rotor harmonic-oscillator model. The enthalpy and entropy functions were computed from the relations given by Mayer and Mayer.[59]

$$(H^o - H_o^o)'' = H^o_{trans} + H^o_{rot} + H^o_{vib} \tag{9}$$

where

$$\frac{H^o_{trans}}{RT} = \frac{5}{2} \tag{10}$$

$$\frac{H^o_{vib}}{RT} = \frac{x}{e^x - 1} \tag{11}$$

$$\frac{H^o_{rot}}{RT} = y_1 \left(1 - \frac{\theta_1}{3T} - \frac{\theta_1^2}{45T^2} - \frac{8\theta_1^3}{945T^3}\right) + y_2 \left(1 - \frac{\theta_2}{3T} - \frac{\theta_2^2}{45T^2} - \frac{8\theta_2^3}{945T^3}\right) \tag{12}$$

and $x = h\nu/kT$, $\theta = h^2/8\pi^2 Ik$, and y_1 and y_2 refer to the mole fractions of N_2^{14} and $N^{14}N^{15}$, respectively.

$$(S^o)'' = S^o_{trans} + S^o_{vib} + S^o_{rot} \tag{13}$$

where

$$\frac{S^o_{trans}}{R} = \frac{5}{2} \ln T + \frac{3}{2} \ln M - 1.164862 \tag{14}$$

$$\frac{S^o_{vib}}{R} = \frac{x}{e^x - 1} - \ln (1 - e^{-x}) \tag{15}$$

$$\frac{S^o_{rot}}{R} = y_1 \left(1 - \ln \frac{2\theta_1}{T} - \frac{\theta_1^2}{90T^2}\right) + y_2 \left(1 - \ln \frac{\theta_2}{T} - \frac{\theta_2^2}{90T^2}\right) \tag{16}$$

The values of the molecular constants used in the above equations are summarized in Table VI. I_1 was calculated from the relation

$$I_1 = h/8\pi^2 c\, B_o \qquad (17)$$

The value of I_2 was computed from the value of I_1 assuming that the equilibrium distance for N^{14}-N^{15} is equal to that for N^{14}-N^{14}.

TABLE VI

MOLECULAR CONSTANTS OF NITROGEN

Description	Symbol	Value	Reference
Atomic Weight	N^{14}	14.00373 c.m.u.	35
Atomic Weight	N^{15}	15.00081 c.m.u.	35
Percent Abundance N^{14}		99.64	35
Percent Abundance N^{15}		0.36	35
Rotational Constant	B_o	1.998 cm^{-1}	31
Fundamental Frequency	ν	2330.72 cm^{-1}	31

8. Experimental Vapor Pressure Data for Nitrogen

A rather large number of investigators have determined the vapor pressure of nitrogen in the liquid range between the triple point (63.152° K) and the normal boiling point (77.347° K). From an examination of the data it appeared that the data of Armstrong,[6] Keesom and Bijl,[52] Giauque and Clayton,[29] and Henning and Otto[38] represented results obtained on several independent temperature scales and also appeared to be of the higher accuracy. The experimental vapor pressure data of these investigators have been compared with the computed values. Other data examined but not included here are the measurements of von Siemens,[81] Cath,[11] Henning,[36] Henning and Heuse,[37] and Aoyama and Kanda.[4]

In addition to the above mentioned vapor pressures, Clusius and Schleich[15] and Kirshenbaum and Urey[56] determined the triple point pressure of N_2^{14} in their study on the vapor pressure of isotopic mixtures.

In the solid nitrogen region ($T \leq 63.152°$ K) the results are more discordant. For this reason all of the vapor pressure data available in the solid region are compared with the calculated results. Investigators who have reported experimental vapor pressure data below the triple point are Giauque and Clayton[29] (54.783° - 63.136° K), Keesom and Bijl[52] (53.264° - 63.146° K), Henning[36] (60.883° - 63.12° K), Aoyama and Kanda[4] (34.69° - 63.1° K), Dokoupil et al[23] (42.1° - 60.5° K), Cath[11] (57.89° - 59.95° K), von Siemens[81] (57.00° - 63.25° K) as reported by Holst,[44] and Borovik et al[9] (21.2° - 26.4° K).

Before comparing the experimental vapor pressure data with the calculated results, the reported temperatures were converted to the thermodynamic temperature scale with a defined ice point of 273.150° K using the methods of correction outlined in Appendix B.

C. Calculation of Vapor Pressures and Heats of Vaporization and Sublimation of Nitrogen

1. Calculations Based on Lennard-Jones (6-12) Potential Function for the Second Virial Coefficient

The vapor pressure and heats of vaporization and sublimation of nitrogen were computed using Equations (5) and (1) and the physical data shown in Table I, from the normal boiling point (77.347° K) to 10° K at one degree intervals. The results are given in Table XVI, Appendix D.

The results are compared with the experimental vapor pressure data in Figures 1, 2A, 3, and 4 by examining the temperature difference $(T_{calc} - T_{obs})$, where T_{obs} is the reported temperature (corrected where possible to an ice point of 273.15° K) corresponding to the experimentally determined pressure, and T_{calc} is the temperature which corresponds to this same pressure as

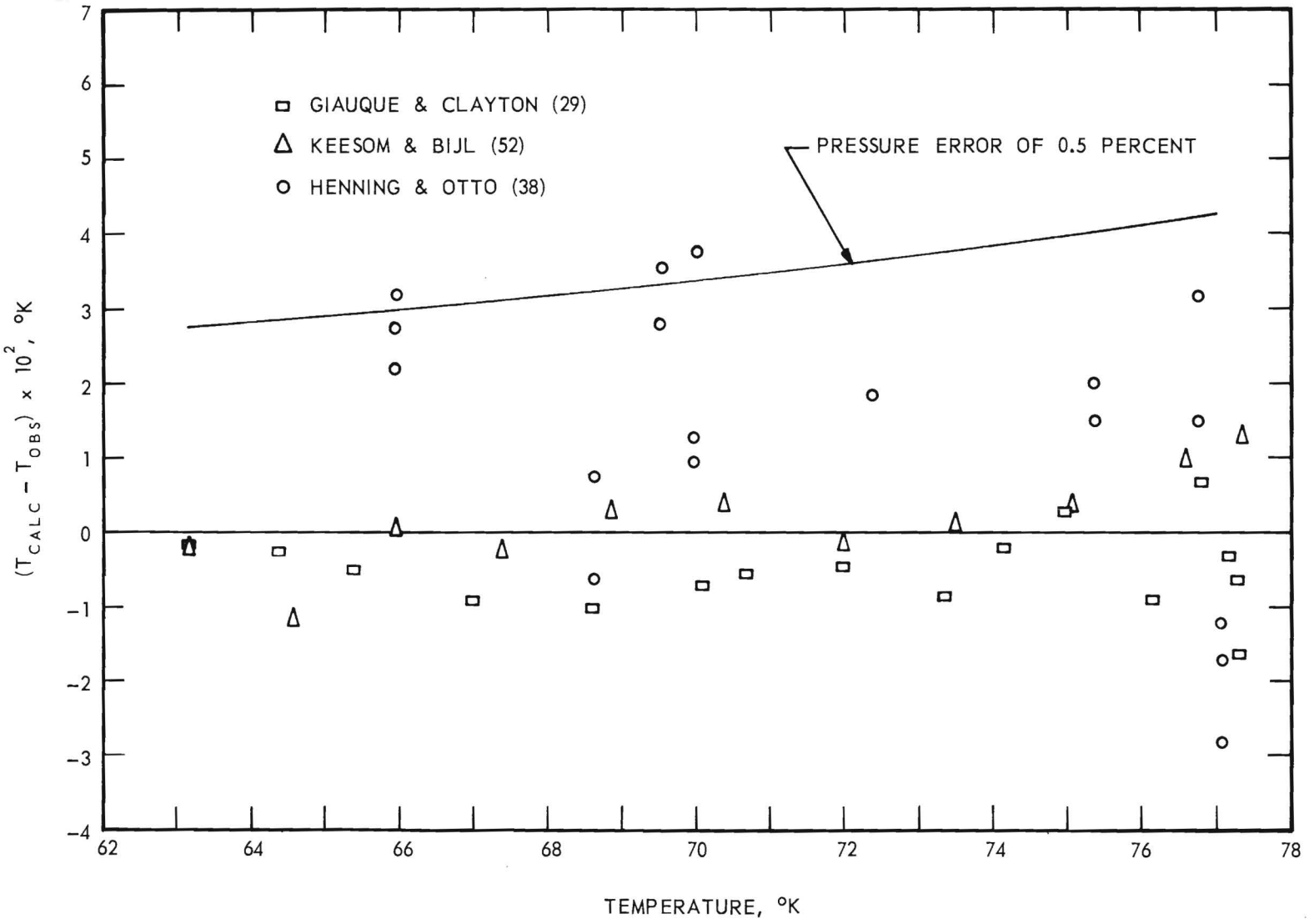

Figure 1. Comparison of Experimental Vapor Pressure Data for Liquid Nitrogen with Computed Results of Table XVI.

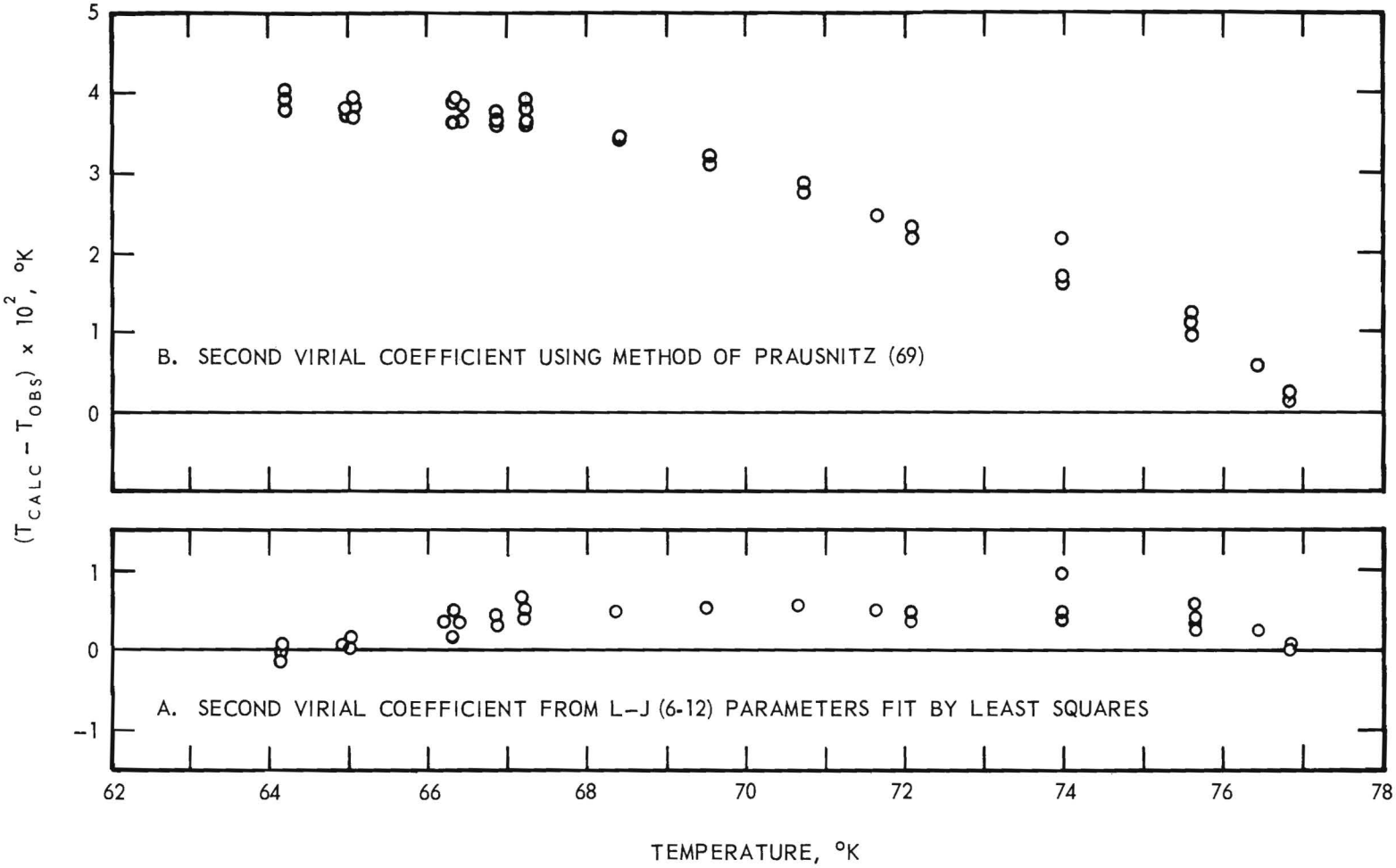

Figure 2. Comparison of Experimental Vapor Pressure Data of Armstrong with Vapor Pressures Computed from Different Second Virial Coefficients.

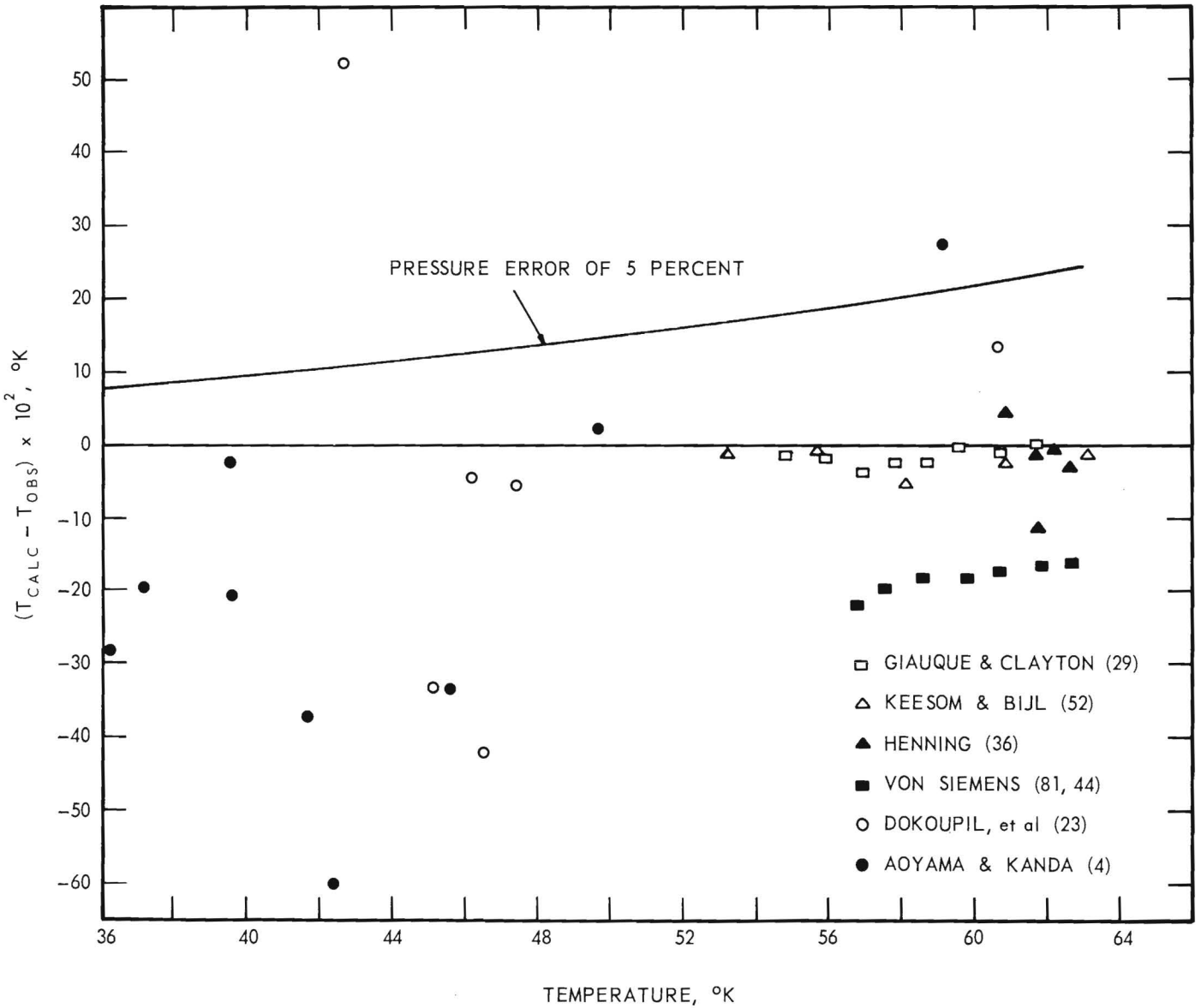

Figure 3. Comparison of Experimental Vapor Pressure Data for Solid β-Nitrogen with Computed Results of Table XVI.

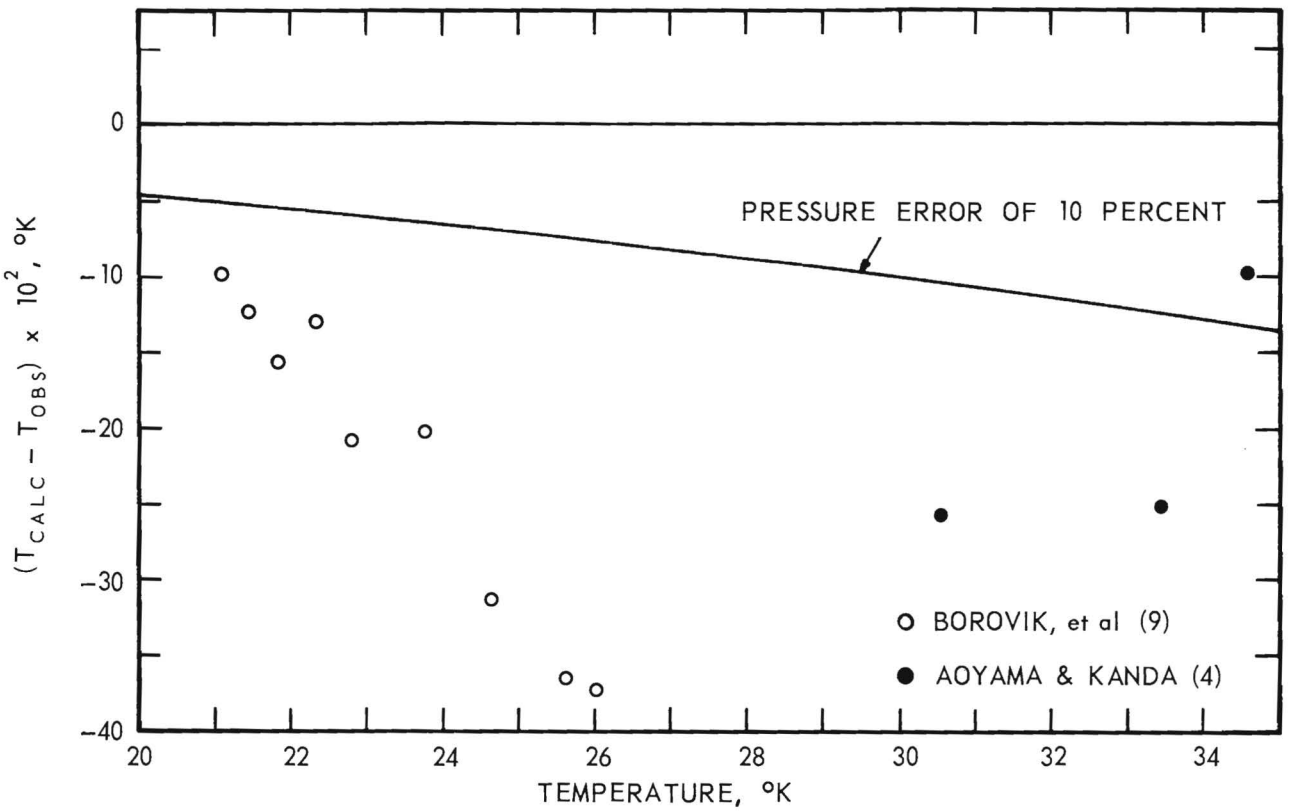

Figure 4. Comparison of Experimental Vapor Pressure Data for Solid α-Nitrogen with Computed Results of Table XVI.

determined by interpolation in Table XVI.* In Figure 1 is shown the deviation of the experimental results of Giauque and Clayton,[29] Henning and Otto,[38] and Keesom and Bijl[52] from the calculated results in the liquid region. The agreement of the results of Giauque and Clayton,[29] and Keesom and Bijl[52] with the calculated results is considered excellent and while the agreement with Henning and Otto[38] is not quite so good, it appears to be within the experimental error of their data which seems to scatter more than the other investigators shown in Figure 1. In Figure 2A the data of Armstrong[6] are compared with the calculated results. These data are shown on separate figures because of the large number of points. Here again the agreement is considered excellent. As can be seen from Figure 2A the data of Armstrong are very consistent. A comparison of the calculated triple point pressure is made with a number of experimental values in Table VII.

In the solid region the data of the various investigators do not agree nearly as well as in the liquid. However, as may be seen from Figure 3, the data of Keesom and Bijl,[52] and Giauque and Clayton[29] agree very well with the computed results as low as they extend. In the very low pressure region only the data of Borovik et al[9] are available. These results and the values of Aoyama and Kanda[4] below the solid transition (35.62° K) are shown in Figure 4.

---

*Values of the calculated temperature corresponding to observed vapor pressures are interpolated from the values shown in Table XVI using Aitken's interative method of polynomial interpolation as described by Milne.[62] This method calculates the value of the dependent variable, in this case 1/T, corresponding to a given value of the independent variable, in this case ln P, by successively interpolation with a 1, 2, 3, . . . , n, n + 1, . . . degree polynomial. In the computer program used here, this successive interpolation was continued until the value of (1/T) computed by the (n + 1) -th degree polynomial differed by less than 1 part in 100,000 from the value computed by the n-th degree polynomial.

TABLE VII

COMPARISON OF TRIPLE POINT PRESSURES OF NITROGEN

Reported Temperature	Pressure (mm Hg)	Year	Investigator
	94.01 ± 0.02	1958	Clusius and Schleich[15]
	93.86 ± 0.02	1942	Kinshenbaum and Urey[56]
63.150° K	94.01 ± 0.05	1937	Keesom and Bijl[52]
-210.015° C	94.6	1936	Henning and Otto[38]
63.136° K	94.01 ± 0.05	1933	Giauque and Clayton[29]
-209.95° C	93.60	1931	Verchoyle[80]
63.09° K	93.91 ± 0.05	1931	Justi[49]
63.152° K	94.12		(Calculated this work)

The experimental pressures of Borovik et al[9] are 20-60 percent smaller than the calculated values.

The values of the heats of vaporization and sublimation are compared with the experimental results of Furukawa and McCoskey[28] in Figure 5. The agreement is considered to be excellent.

2. Calculations Based on the Kihara Core Model for the Second Virial Coefficient

Computations of the vapor pressure and heats of vaporization were made in the same manner as described in the previous section except that the second virial coefficient was represented by the Kihara[54] core model with additional corrections for the quadrupole interactions. The method of calculation and the constants for the potential function were taken from Prausnitz[69] and is discussed further in Appendix C.

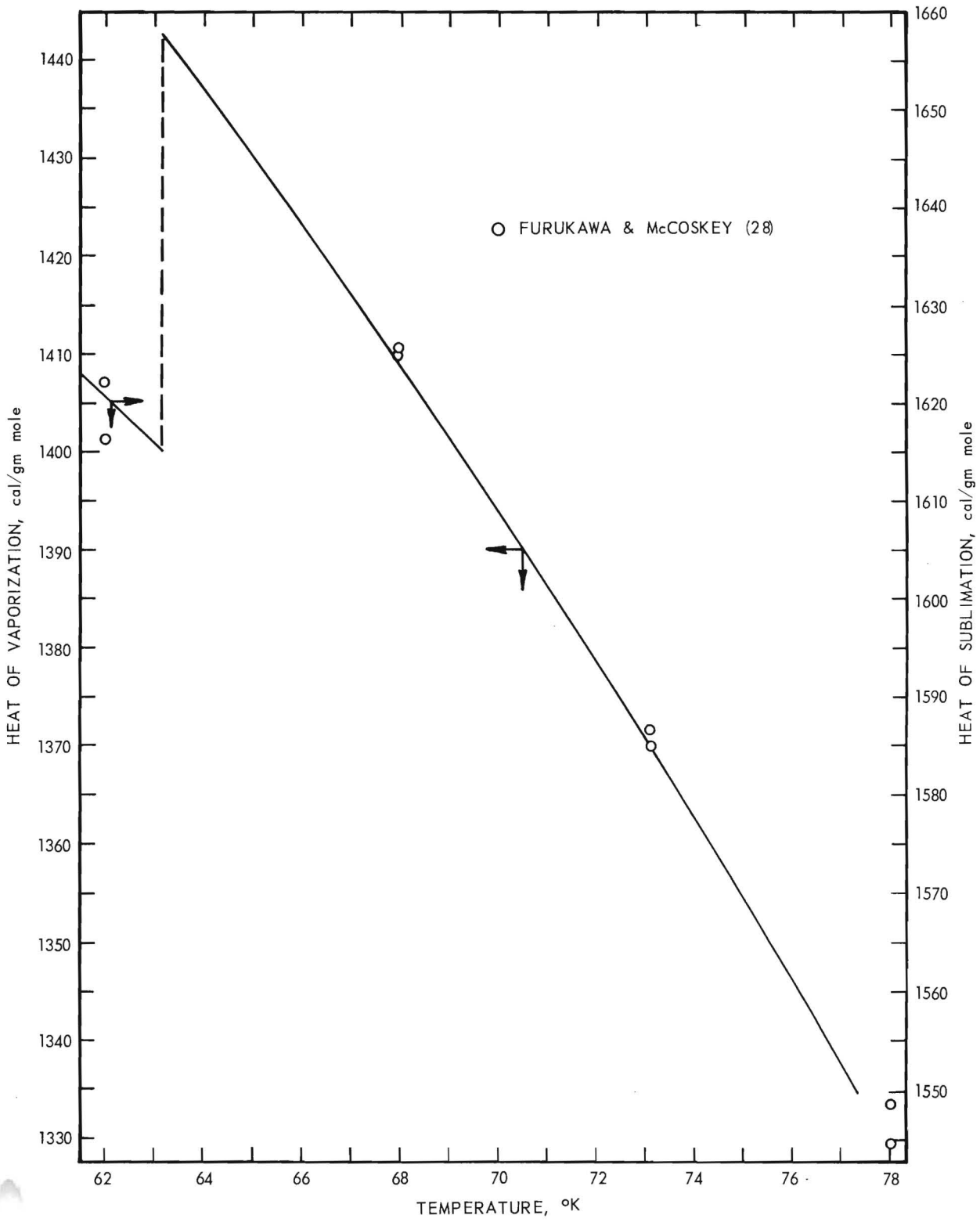

Figure 5. Comparison of Experimental Heats of Vaporization and Sublimation for Nitrogen with Computed Results of Table XVI.

The results obtained using the Kihara core model with the parameters of Prausnitz[69] for nitrogen do not agree with the experimental vapor pressure data as well as do the results computed using the simpler Lennard-Jones (6-12) intermolecular potential function with the parameters (ϵ/k = 90.467° K, b_o = 76.869 cc/gm mole) obtained as described in Appendix C. A comparison of the results computed using the two different models for the second virial coefficient is shown in Figures 2A and 2B, where the experimental vapor pressures of Armstrong[6] are compared with the calculated results. It is to be noted however that in spite of this difference the computed vapor pressures at 20° K, 1.006×10^{-11} mm Hg and 1.085×10^{-11} mm Hg for the Kihara core model and the Lennard-Jones model, respectively, are in good agreement.

D. Third Law Calculation for Nitrogen

Giauque and Clayton[29] calculated the calorimetric entropy of the ideal gas at the normal boiling point of nitrogen (77.32° K) and one atmosphere pressure using their own calorimetric data. They obtained a value of 36.53 e.u. They also computed a value of 36.416 e.u. for the entropy of the ideal gas at 1 atmosphere pressure from spectroscopic data.

A new value of the calorimetric entropy has been computed using the data presented in Table I, that is, the data used in the computation of the vapor pressure and heats of vaporization and sublimation. In order to make this computation it was necessary to extrapolate the heat capacity data to 0° K. This was done by fitting a Debye function for five degrees of freedom to the heat capacity calculated from the heat capacity polynomial at 10° K. A small correction for $(c_s' - c_v')$ of 0.006 cal/gm mole-°K was made by assuming the Lindemann melting point relation. The results are shown below in Table VIII compared to the spectroscopic entropy obtained from Equation (13).

TABLE VIII

THIRD LAW CALCULATION FOR NITROGEN

0° - 10° K (θ_D = 82.3° K, 5 deg. of freedom)	0.451
10°-35.62° K	6.026
35.62° K (ΔH_{tr} = 54.71 cal/g mole)	1.536
35.62° - 63.152° K	5.593
63.152° (ΔH_f = 172.30 cal/g mole)	2.728
63.152° - 77.347° K	2.732
77.347° (ΔH_v = 1334.8 cal/g mole)	17.257
Entropy of real gas at 1 atm	36.323
Correction for non-ideality	0.146
Entropy of ideal gas at 1 atm	36.469
Spectroscopic Entropy from Equation (13)	36.386

E. Recommended Values for the Vapor Pressure and Heats of Vaporization of Nitrogen between 77.347° (n.b.p.) and 10° K

The excellent agreement between the computed values for the vapor pressure given in Table XVI and the experimental data of Giauque and Clayton,[29] Armstrong,[6] and Keesom and Bijl[52] in the liquid and solid range suggest that the computed values may well represent the experimental data within the accuracy of the temperature scales used by these investigators. The computed values are therefore recommended as smoothed values, especially in the solid range below 50° K where the available experimental data are scattered and discordant.

IV. VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF FLUORINE

A. Introduction

The vapor pressure and heats of vaporization and sublimation of fluorine were calculated from the normal boiling point (85.03° K) to 14° K using the appropriate equations from Section II of this report. In the case of fluorine the calculations were essentially the same as those made for nitrogen. Fluorine was considered to consist of the single isotope F^{19}. Whereas in the calculations of the vapor pressure and heats of vaporization and sublimation of nitrogen there was a large amount of data from which to select the initial parameters, in the case of fluorine there was usually very little choice. Indeed most of the data available on fluorine was obtained by Johnston and Coworkers at Ohio State University.

B. Review of Experimental Data for Fluorine

The calculation of vapor pressures from Equation (5) and heats of vaporization and sublimation from Equation (1) in the temperature range from the normal boiling point to 14° K made use of the same type of data as for nitrogen, namely: $(\Delta H_v)_{T_l}$; P_l; T_l; (ΔH_{tr}); T_{tr}; and c_s' and v_s' as a function of temperature. A representation of the second virial coefficient as a function of temperature was also required. The effect of higher virial coefficients was assumed to be negligible. In addition, the appropriate molecular structure data were required to permit calculation of the thermodynamic properties of the ideal gas.

From a survey of the literature, a selection has been made of the "best" values of these thermal and related properties of fluorine. These selected values are summarized in Table IX. The basis for their selection is discussed in the following sections. The available experimental data for the vapor

TABLE IX

SUMMARY OF SELECTED PHYSICAL PROPERTIES OF FLUORINE

Property	Selected Value	Reference or Table No.
Normal boiling point (n.b.p.) (P = 760 mm Hg)	85.03° K	X
Triple point (t.p.)	53.54° K	45
Solid Transition Temperature	45.55° K	45
Heat of Vaporization	1561.3 cal/gm mole	XI
Heat of Fusion (t.p.)	121.98 cal/gm mole	XI
Heat of Solid Transition	173.90 cal/gm mole	XI
Heat Capacity of Saturated Condensed Phases	Appropriate Polynomial	XII
Mean Molal Volume of Liquid (53.54° - 85.03° K)	24.57 ml/gm mole	44
Mean Molal Volume of Solid	20 ml/gm mole	
Lennard-Jones (6-12) Parameters for Second Virial Coefficients	ϵ/k = 125.71° K b_o = 59.265 cc/gm mole	
Molecular Parameters		XIII
Moment of Inertia	3.17×10^{-39} gm-cm^2	
Fundamental Frequency	891.0 cm^{-1}	
Molecular Weight	38.00	

pressure of solid and liquid fluorine below one atmosphere have been assembled for comparison with the computed results.

Although in general the temperature measurements are not of sufficient accuracy to warrant any conversion to a consistent ice point of 273.15° K, such conversion was made for the normal boiling point, heat of transition and the experimental vapor pressure data. However the selected values of the temperatures are quoted only to the nearest 0.01° K. The methods of conversion of the temperatures are given in Appendix B.

1. Phase Transition Temperatures of Fluorine

(a) Normal Boiling Point

The normal boiling point of fluorine has been reported by several investigators whose values are summarized below in Table X. Of these the most reliable data appear to be those of Hu, White and Johnston,[45] and Cady and Hildebrand.[10]

TABLE X

NORMAL BOILING POINT OF FLUORINE

Reported Temperature (°K)	Ice Point (°K)	Corrected Temperature T_o = 273.15° K	Investigator
85.02 ± 0.02[a]	273.16	85.03 ± 0.02	Hu et al[45]
84.93 ± 0.01	273.10	84.95 ± 0.1	Cady and Hildebrand[10]
85.21 ± 0.1[b]		85.28 ± 0.1	Claussen[13]
85.19	273.20	85.17	Aoyama and Kanda[5]
Selected Value		85.03	

[a] There appeared to be a slight error in the reported value of 85.02° K. Calculations indicated that 85.03° K is consistent with their vapor pressure equation.

[b] Temperatures were measured using the vapor pressure of oxygen and the vapor pressure relation of Cath.[11] The reported value was corrected by calculating the equivalent pressure of oxygen, converting this pressure to a temperature using the more recent vapor pressure data of Hoge[41] and finally correcting to an ice point of 273.15 as outlined in Appendix B.

Hu, White and Johnston[45] reported a value of 85.02° ± 0.02° K. This value was reported to have been determined from their vapor pressure equation which adequately represented their data at the boiling point. Calculation from their vapor pressure equation indicated this number should be 85.03° K. Melting point determinations indicated the purity of the sample to be 99.97 percent.

Temperatures were measured using a copper-constantan thermocouple calibrated against a helium gas thermometer.

Cady and Hildebrand[10] used a fluorine sample that exhibited a constant boiling point with batch distillation. No estimate of the purity is made. The temperature measurements were made using copper-constantan thermocouples made of wire from the same spool as used and calibrated by Giauque et al.[30] Temperature measurements were believed to be reproducible to 0.05° K.

The value selected in the present work was that of Hu, White and Johnston.[45]

(b) Triple Point of Fluorine

The best value of the triple point temperature appears to be that of Hu, White and Johnston[45] (53.54° K). Several determinations were made in conjunction with the evaluation of the sample purity. The only other value of the melting point found was that reported by Kanda[50] (55.2° K).

(c) Solid Transition Temperature

Hu et al[45] have reported a solid phase transition in fluorine at 45.55° K. Kanda[50] in earlier measurements did not observe this transition.

2. Heats of Transition of Fluorine

All values of the heats of transition were taken from the work of Hu, White and Johnston.[45] The only other value reported for any of the heats of transition was the calorimetrically determined heat of fusion reported by Kanda.[50] These values are given below in Table XI.

3. Heat Capacity of Saturated Condensed Fluorine

Hu, White and Johnston[45] have determined the heat capacity of saturated condensed fluorine from 13.89° - 81.32° K. Measurements of the heat capacity have also been made by Kanda,[50] but the results are in substantial

TABLE XI

HEATS OF TRANSITION OF FLUORINE

Reported Temperature (°K)	Value (cal/gm mole)	Investigator
	-- Heat of Vaporization --	
84.71	1563.98 ± 3	Hu, White and Johnston[45]
85.03	1561.3	(Above value corrected to n.b.p. using Equation (1)).
Selected Value	1561.3	
	-- Heat of Fusion --	
53.54	121.98 ± 0.5	Hu, White and Johnston[45]
55.2	372	Kanda[50]
Selected Value	121.98	
	-- Heat of Solid Transition --	
45.55	173.90 ± 0.04	Hu, White and Johnston[45]
Selected Value	173.90	

disagreement with the data of Hu et al[45] and in fact fail to account for the solid transition. The data of Hu et al[45] were fitted to three equations of the form of Equation (8) by the method of least squares. The resulting coefficients are given below in Table XII.

TABLE XII

COEFFICIENTS OF HEAT CAPACITY POLYNOMIALS FOR FLUORINE

Range (°K)	A_o	$A_1 \times 10^1$	$A_2 \times 10^2$	$A_3 \times 10^3$	$A_4 \times 10^5$
14.0 -45.55	2.1964724	-4.9535548	4.6020823	-1.1499697	1.0291439
45.55-53.54	-5.6382020	5.6500849	-0.43269337	0	0
53.54-85.03	19.536620	-1.7486857	0.12839854	0	0

4. Molal Volumes of Saturated Condensed Fluorine

(a) Liquid Fluorine

Several recent determinations of the density of liquid fluorine have been reported.[44,82,24,55] The various sets of data are in good agreement. The maximum deviation among the various sets of data was estimated to be ±0.3 percent from a graph of the experimental data. The data of Jarry and Miller[48] were chosen as representative, and a value of the mean molal volume of liquid fluorine for the temperature range 53.53° to 85.03° K was calculated to be 24.57 ml/gm mole which corresponds to a temperature of 79.39° K. The density of the saturated liquid at the triple point was estimated to be 1.705 gm/cc.

(b) Solid Fluorine

No reliable data are available for the density of solid fluorine. A value of 1.3 gm/cc is reported in the International Critical Tables,[46] but no temperature or reference is quoted. This value appears to be considerably low based on the value of the liquid density. The value of the density of the solid was assumed to be 10 percent higher than that of the liquid at the triple point. This results in a value of 20 ml/gm mole for the molal volume.

6. Second Virial Coefficient and Lennard-Jones (6-12) Parameters

The only available experimental second virial coefficient data for fluorine were determined by White, Hu and Johnston.[83] Their values were determined by measurement of low pressure P-V-T values using an apparatus which was essentially a constant volume gas thermometer. The calorimeter was filled at about 300° K with a filling pressure of approximately one atmosphere. Temperatures were read with a thermocouple calibrated against a helium gas thermometer and pressures were said to be reproducible to ± 0.03 mm Hg. The

P-V-T relation was assumed to be represented by

$$PV = RT + BP \qquad (18)$$

Values of B were used by them to obtain values of the Lennard-Jones (6-12) parameters. The values found by White et al[83] were $e/k = 121 \pm 3°$ K, and $r_o = 3.61 \pm 0.04$ Å ($b_o = 59.35$ cc/g mole).

The constants for the Lennard-Jones (6-12) intermolecular potential were redetermined by the least squares method described in Appendix C for nitrogen, using the values of B reported by White et al.[83] The values obtained were $e/k = 125.71°$ K, and $b_o = 59.265$ cc/gm mole. This procedure weighted all data equally including the data at 80° and 85° K. The experimental values of the second virial coefficient and the values computed from the two sets of Lennard-Jones parameters are compared in Figure 6. It will be noted that the two calculated curves show significant deviation, the parameters of White et al giving on the whole the better agreement with the experimental data. However, because the least squares fit parameters give a slightly better fit of the virial coefficient data in the temperature range of interest ($T < 85°$ K) these parameters have been selected for use in the vapor pressure calculations.

6. Thermodynamic Functions of the Ideal Gas

The thermodynamic properties of fluorine in the ideal gas state were computed using the same equations, (9) - (17), as were used for nitrogen. In Equations (12) and (16) the mole fraction of F^{19} is unity since there are no other naturally occurring stable isotopes. The values of the molecular constants used were the same as used in the recent JANAF Tables[47] of the thermodynamic properties of various gases. These were based on values calculated from

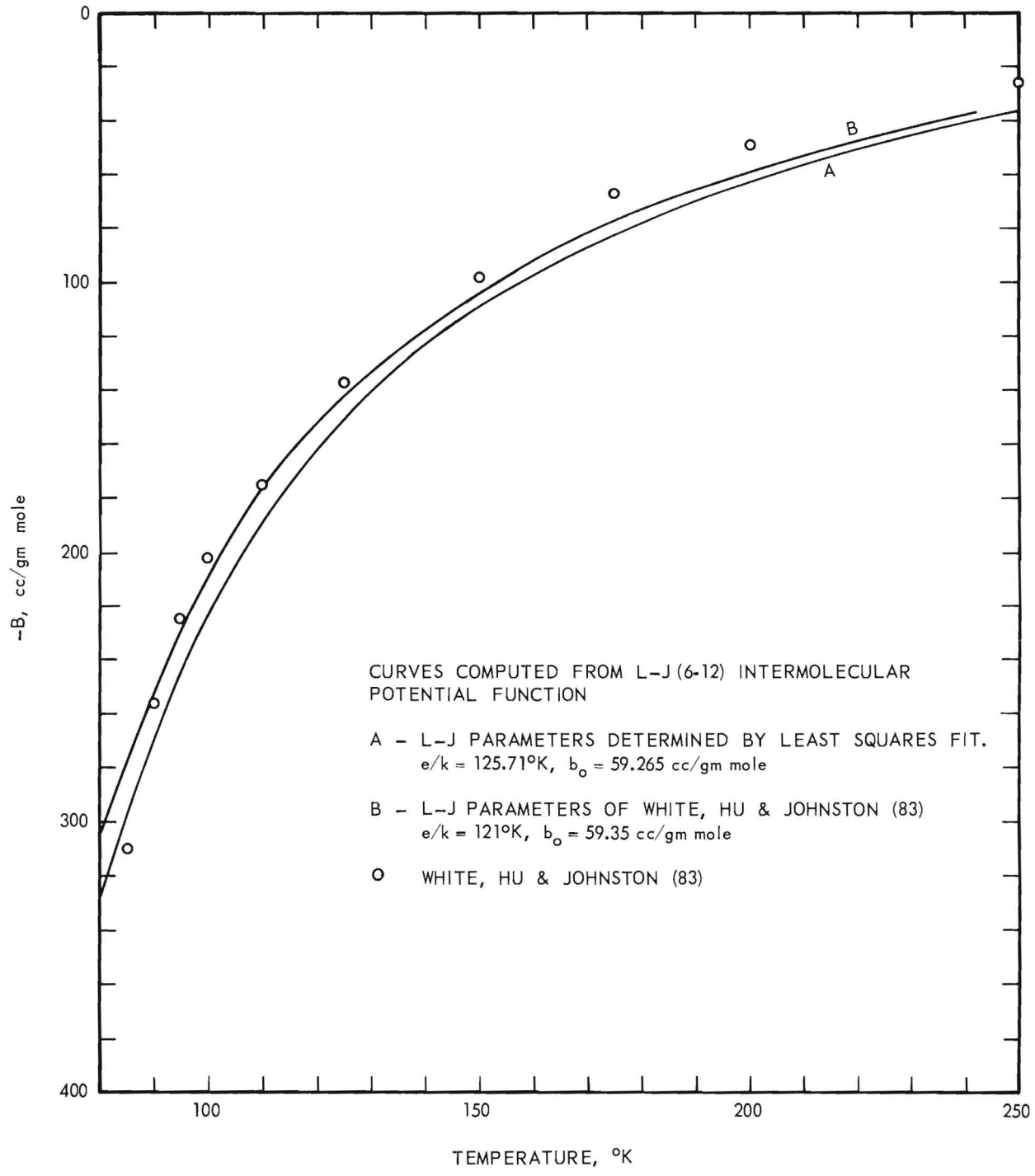

Figure 6. Second Virial Coefficient of Fluorine.

the Raman measurements of Andryckuk[2] and the disassociation energy listed by Stamper and Barrow.[79] The results are summarized below in Table XIII.

TABLE XIII

MOLECULAR CONSTANTS FOR FLUORINE[77]

Description	Symbol	Value
Rotational Constant	B_o	0.8828 cm^{-1}
Fundamental Frequency	ν	891.0 cm

8. Experimental Vapor Pressure Data for Fluorine

(a) Solid Fluorine

The only experimental values for the vapor pressure of solid fluorine are those of Aoyama and Kanda.[5] They report only five values in the range 51.85° - 55.15° K.

(b) Liquid Fluorine

The vapor pressure of liquid fluorine has been determined by Hu, White, and Johnston[45] (53.56° - 89.40° K), Cady and Hildebrand[10] (72.53° - 85.99° K), Claussen[13] (58° - 85° K) and Aoyama and Kanda[5] (59.90° - 86.21 ° K). Claussen does not give his experimental data, but reports the results of 140 determinations as

$$\text{Log}_{10} P(\text{cm}) = -\frac{462.66}{T} + 8.7202 - 0.01656\ T \qquad (19)$$

Claussen reports that this equation fits all data within 0.15° K and three-fourths of his data deviate by less than 0.10° K.

C. Calculation of Vapor Pressure and Heats of Vaporization and Sublimation of Fluorine

1. Calculations Based on Second Virial Coefficient Computed Using Least Squares Values of Lennard-Jones (6-12) Parameters

The vapor pressure and heats of vaporization and sublimation of fluorine were computed using Equations (5) and (1) and the physical data shown in Table IX, from the normal boiling point (85.03° K) to 14° K at one degree intervals. The results are given in Table XVII, Appendix D.

The results are compared with the experimental vapor pressure data in Figure 7 by examining the temperature difference $(T_{calc} - T_{obs})$, where T_{obs} is the reported temperature (corrected where possible to an ice point of 273.15° K) corresponding to the experimentally determined pressure and T_{calc} is the temperature which corresponds to this same pressure as determined by interpolation in Table XVII. The method of interpolation was the same as used for nitrogen. In Figure 7 the agreement between the calculated results and the data of Hu, White and Johnston[45] is seen to be excellent from the boiling point to about 60° K. Below this the deviation is quite large and unexplained. It is noted that, although the error in terms of temperature deviations is quite large below 60° K, the corresponding error in terms of pressure varies from about 0.13 mm Hg to 0.25 mm Hg.

The five experimental measurements in the range 51.85° - 55.15° K of Aoyama and Kanda[5] differ from the calculated values by several degrees and are not shown in Figure 7.

2. Calculations Using Lennard-Jones (6-12) Parameters of White, Hu and Johnston[83]

The vapor pressure calculations made in the preceding section were

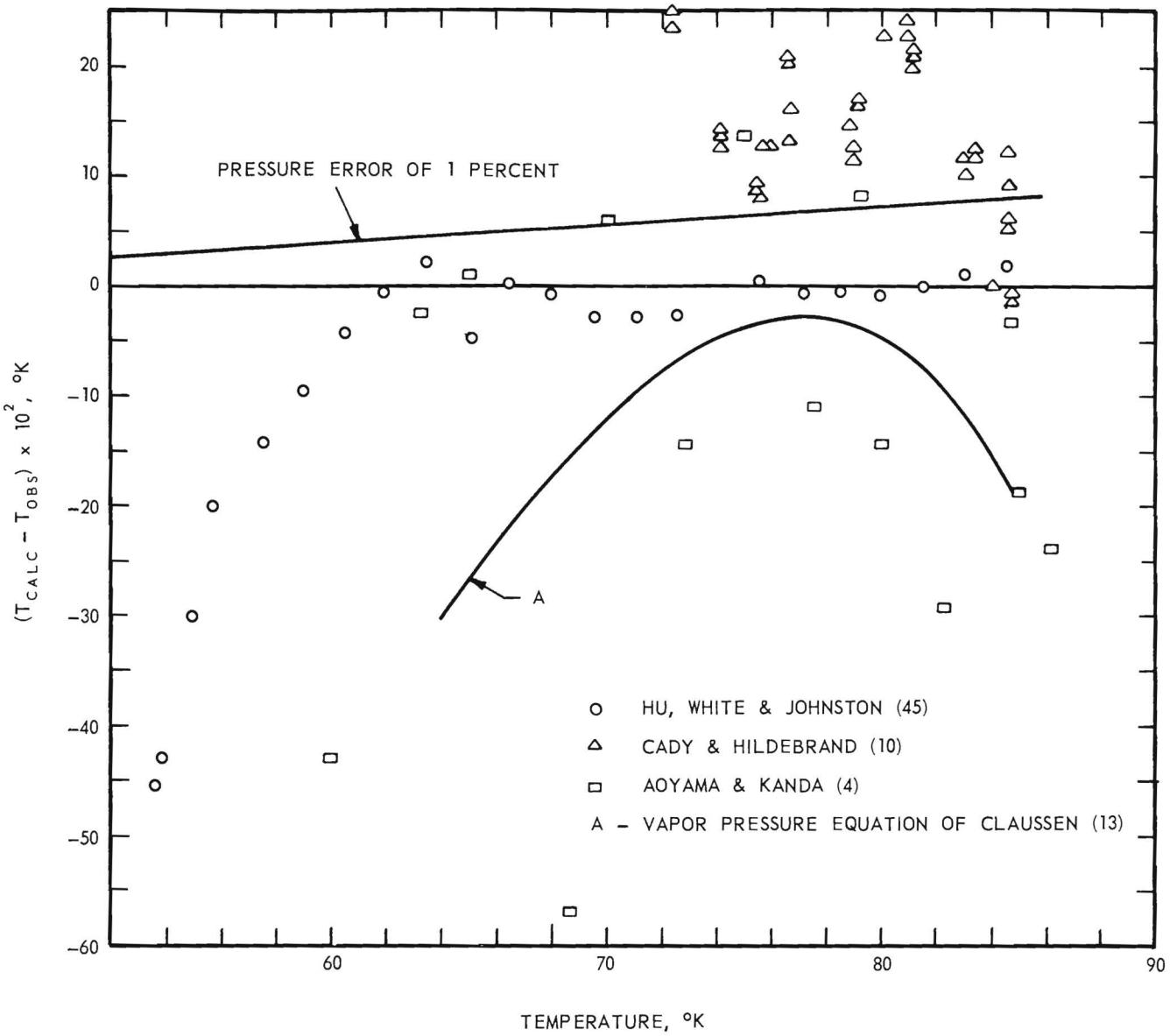

Figure 7. Comparison of Experimental Vapor Pressure Data for Liquid Fluorine with Computed Results of Table XVII.

repeated using the same input values except that the e/k and b_o (121° K, 59.35 cc/gm mole) of White et al[83] were used. Above the triple point the vapor pressures calculated using these parameters do not differ significantly from those computed in the preceding section; at 20° K the vapor pressure is about 3 percent higher and at 14° K about 5 percent higher.

D. Third Law Calculation for Fluorine

The calorimetric entropy of fluorine has been computed by Hu, White and Johnston[45] to be 39.58 ± 0.16 e.u. at their choice of the normal boiling point (85.02° K). This calculation, based on the applicability of the third law of thermodynamics, involved an extrapolation of the heat capacity data below 13.89° K. The value obtained for the calorimetric entropy was compared to the statistically computed value for the ideal gas at one atmosphere pressure of Cole, Farber and Elverum[17] (39.62 ± 0.02 e.u.) and Haar and Beckett[34] (39.56 ± 0.01 e.u.).

The calorimetric and statistical entropy of the ideal gas have been recomputed by us using the same data (i.e., Table IX) as was used in the vapor pressure and heat of vaporization and sublimation calculations. The heat capacity of the condensed phase below 14° K was assumed to follow a Debye function. The θ_D used in the calculations was obtained from the value of the heat capacity at 14° K given by the least square polynomial. The value of θ_D found, assuming five degrees of freedom, was 107.9° K. The value of the calorimetric entropy of the ideal gas at 85.03° K and one atmosphere pressure was found to be 39.379 e.u. The results are given in Table XIV. The value of the entropy of the ideal gas at one atmosphere pressure computed from Equation (16) was found to be 39.566 e.u. Most of the disagreement (0.20 e.u.) between the calorimetric entropy reported here, and that reported by Hu, White and Johnston is in the correction for the non-ideality of the gas and the extrapolation below 14° K.

TABLE XIV

THIRD LAW CALCULATION FOR FLUORINE

0 - 14° K (θ_D = 107.9° K, 5 deg. of freedom)	0.544
14°-45.55° K	5.996
45.55° K (ΔH_{tr} = 173.9 cal/gm mole)	3.818
45.55°-53.54° K	1.890
53.54° K (ΔH_f = 121.98 cal/gm mole)	2.278
53.54°-85.03° K	6.333
85.03° K (ΔH_v = 1561.3 cal/gm mole)	18.362
Entropy of real gas at 1 atm	39.221
Correction for non-ideality	0.158
Entropy of Ideal gas at 1 atm	39.379
Spectroscopic Entropy from Equation (16)	39.566

E. Recommended Values for Vapor Pressure and Heats of Vaporization and Sublimation of Fluorine in the Range 85.03° (n.b.p.) and 14° K

The generally good agreement found between the computed vapor pressures (Table XVII, Appendix D) and the experimental data of Hu, White and Johnston[45] for liquid fluorine suggest that their vapor pressure data are consistent with their thermal measurements. Admittedly the agreement is poorer below 60° K. The limited measurements of other investigators, which appear to be less accurate and more scattered than those of Hu et al[45], show significant disagreement with the computed values. In view of the limited and scattered nature of the experimental data for fluorine, it is recommended that the computed vapor pressures given in Table XVII be used as a smoothed representation of the vapor pressure of fluorine, especially below the triple point.

V. ACKNOWLEDGEMENTS

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VII. APPENDIXES

A. Nomenclature and Physical Constants*

B = second virial coefficient of gas.

B_i = second virial coefficient calculated from Equation (28) at T_i.

$\overline{B}_i$ = experimental second virial coefficient at T_i.

B^* = reduced second virial coefficient = B/b_o.

$b^{(j)}$ = coefficients in Lennard-Jones (6-12) second virial series (See Equation (28)).

B_o = $h/8\pi^2 cI = 2.79832 \times 10^{-39}/I$ (gm-cm^2).

b_o, e/k = parameters used in the Lennard-Jones (6-12) intermolecular potential function.

c = velocity of light = 2.99702×10^{10} cm/sec.

c_s' = molal heat capacity of saturated condensed phase.

F_1, F_2, F_3 = functions in the Kihara core model for the second virial coefficient, defined by Equation (37).

G^* = function defined by Equation (32).

H_{10} = function for quadrupole interaction, defined by Equation (42).

h = Planck constant = 6.62377×10^{-27} erg-sec/molecule.

$(\Delta H_v)_T$ = heat of vaporization (or sublimation) at T.

(ΔH_{tr}) = heat of transition of condensed phase at transition temperature, T_{tr}.

$\sum_{T}^{T_1} (\Delta H_{tr})$ = sum of all condensed phase transitions from T to T_1.

*The physical constants used were those of Rossini et al, J. Am. Chem. Soc. 74, 2699 (1952) adjusted to an ice point of 273.150° K.

$(H^{o} - H_{o}^{o})_{T}^{''}$ = enthalpy function for ideal gas at T.

I = moment of inertia.

k = Boltzmann constant = 1.380308×10^{-16} erg/°K-molecule.

M = molecular weight.

M_{o}, S_{o}, V_{o} = parameters of Kihara core model.

N_{o} = Avogadro's Number = 6.02380×10^{23} molecules/gm mole.

P = pressure.

P_{1}, T_{1} = pressure and temperature of a fixed point on the vapor pressure curve.

Q = molecular quadrupole moment.

Q^{*} = reduced quadrupole moment (dimensionless).

R = gas constant = 1.98726 cal/gm mole °K = 0.0820574 liter atm/gm mole °K. (1 calorie = 4.1840 ab. joules = 4.1833 int. joules).

$S^{o}(P,T)^{''}$ = entropy of the ideal gas at P and T.

$(S^{o})_{T}^{''}$ = entropy of ideal gas at P = 1 atm and T.

T = temperature on the thermodynamic scale with a defined ice point of 273.15° K.

T^{*} = temperature on the Kelvin Scale used by individual investigator.

t^{*} = temperature on the Celsius Scale used by individual investigator.

t = degree Celsius.

U = potential energy between molecules.

U_{o} = minimum potential energy between molecules.

V = molal volume of gas.

$v_{s}^{'}$ = molal volume of saturated condensed phase.

Z = U_{o}/kT.

δ = defined by Equation (2) and Equation (4).

ϵ = defined by Equation (6) and Equation (7).

θ = $h^2/8I\pi^2k$, also = e/kT (Equation 28).

ν = fundamental frequency of diatomic molecule.

ρ = shortest distance between molecular cores.

ρ_o = shortest distance between molecular cores at minimum potential energy.

σ = separation of molecular centers at zero potential energy.

Superscripts

' = condensed phase.

'' = gas phase

* = refers to temperature scale of individual investigator. Also refers to reduced state, i.e, $B^* = B/b_o$.

Subscripts

O_2 = normal boiling point of oxygen.

o = ice point.

s = saturated vapor or condensed state.

v = vaporization. Also refers to sublimation for temperatures at and below the triple point.

f = fusion.

nbp = normal boiling point.

tp = triple point.

B. Conversion of Temperature Scales

The conversion of temperatures reported by a given investigator to a consistent thermodynamic scale based on an ice point of 273.150° K has been made where possible. The "best" value for the normal boiling point of oxygen on this scale has been taken to be 90.168° K, the value selected by van Dijk.[75] The various methods used for making these corrections are given below. The final

corrected thermodynamic temperature (in °K) used in this paper is represented by T; the temperature reported by the investigator is represented by T^*. In cases where the original temperatures were reported in °C, these were converted to T^* by addition to the reported ice point T_o^*. When no ice point was given, the reported temperature in °C was added to 273.150° to obtain T in °K.

The relations used for making temperature scale conversions were:

1. Methods involving only ice point ratios

$$T = T^*(T_o/T_o^*) \qquad (20)$$

$$T = T^*(273.15/273.16) \qquad (21)$$

$$T = T^*(273.15/273.10) \qquad (22)$$

$$T = T^*(273.15/273.144) \qquad (23)$$

$$T = T^*(273.15/273.20) \qquad (24)$$

This method of conversion of a thermodynamic temperature scale from one ice point to another is strictly correct only if the ice point temperature is a defined point. When T_o is obtained from a gas thermometer scale defined at the ice point and normal boiling point of water, a more complicated relation is required for exact conversion. (See, for instance, van Dijk).[75] Data for making the exact conversions are not always given by the investigator. However, the exact relations reduce to the simple relation used here in the first approximation. Henning and Otto[38] have used a somewhat different approximate method for correction. Their relation gave the same results as Equation (20) to about 0.002°.

2. Methods involving only oxygen point

$$T = T^*(T_{o_2}/T_{o_2}^*) \qquad (25)$$

$$T = T^*(90.168/90.190) \qquad (26)$$

C. Second Virial Coefficient and Lennard-Jones (6-12) Parameters for Nitrogen

1. Lennard-Jones (6-12) Intermolecular Potential Function

The available experimental second virial coefficient data for nitrogen were used to obtain the Lennard-Jones (6-12) intermolecular potential function using a least square method described below. Table XV summarizes the data used in the calculation. The second virial coefficients of Nijhoff[65] were obtained from the P-V-T data of Onnes and van Urk.[66] The virial coefficients reported by van Itterbeek et al[77] are based on sound velocity measurements and the second virial coefficients determined at higher temperatures based on the P-V-T data of Onnes and van Urk.[66] The second virial coefficients of Cath and Onnes[12] were determined by comparing the characteristics of a nitrogen-filled gas thermometer to those of one filled with hydrogen.

Only the data up to a temperature of 100° C were used in the least squares fit.

TABLE XV

SOURCES OF EXPERIMENTAL SECOND VIRIAL COEFFICIENTS FOR NITROGEN

Range (°K)	Number of Data Points Used in Least Square Fit	Investigator
69.57 - 241.40	14	Cath and Onnes[12]
80.02 - 299.99	12	Friedman[27]
143.15 - 673.15	6	Holborn and Otto[43]
126.83 - 293.15	11	Nijhoff[65]
65.00 - 150.00	9	van Itterbeek, et al[77]
273.15 - 423.15	5	Otto, Michels and Wouters[67]
273.15 - 423.15	5	Michels, et al[60]

The values of e/k (90.467° K) and b_o (76.869 cc/gm mole) were obtained using 62 data points from the references of Table XV. The calculational procedure minimized the sum of the squares of the residuals, where the residual is defined as

$$R_i = (\overline{B}_i - B_i) \tag{27}$$

and $\overline{B}_i$ and B_i are the experimental and calculated second virial coefficients respectively at T_i. Values of B_i were obtained from the series expansion of the Lennard-Jones (6-12) intermolecular potential function given by Hirschfelder, Curtiss, and Bird[40] as a function of θ ($\theta = e/kT$).

$$B_i^* \equiv \left(\frac{B_i}{b_o}\right) = \sum_{j=0}^{\infty} b^{(j)}\ \theta_i^{(1+2j)/4} \tag{28}$$

The values of $b^{(j)}$ are tabulated by Hirschfelder et al[40] for j = 0, 1, . . . 40. Applying the conditions of the least square assumption for N data points, namely,

$$\frac{\partial}{\partial b_o}\left(\sum_{i=1}^{N} R_i^2\right) = 0 \quad \text{and} \quad \frac{\partial}{\partial (e/k)}\left(\sum_{i=1}^{N} R_i^2\right) = 0 \tag{29}$$

the two "normal" Equations (30) and (31) are obtained.

$$\left(\sum_{i=1}^{N} \overline{B}_i B_i^*\right) \Big/ \left(\sum_{i=1}^{N} (B_i^*)^2\right) = b_o \tag{30}$$

$$\sum_{i=1}^{N} \left(\overline{B}_i - b_o B_i^*\right)\left(b_o \frac{\partial B_i^*}{\partial (e/k)}\right) = 0 \tag{31}$$

Defining

$$G_i^* = \sum_{j=0}^{40} \left(\frac{1+2j}{4}\right) b^{(j)} \theta_i^{(1+2j)/4} \tag{32}$$

then

$$\frac{\partial B_i^*}{\partial (e/k)} = G_i^*/(e/k) \tag{33}$$

Equation (30), which is a function of (e/k) only, may be substituted into Equation (31) and from the definition of G_i^* the result rewritten as

$$\left(\sum_{i=1}^{N} \bar{B}_i B_i^*\right)\left(\sum_{i=1}^{N} B_i^* G_i^*\right) - \left(\sum_{i=1}^{N} \bar{B}_i G_i^*\right)\left(\sum_{i=1}^{N} (B_i^*)^2\right) = 0 \tag{34}$$

The value of e/k is then found by iterative solution of Equation (34). Once the value of e/k is found the corresponding value of b_o is obtained from Equation (30). Care should be exercised in the solution of Equation (34) since more than one solution is sometimes possible.

2. Kihara Core Model with a (6-12) Intermolecular Potential Function

Kihara[54] has derived general expressions for the second virial coefficient of gases assuming an impenetrable core for the gas molecule rather than the point center model used in the Lennard-Jones model. This core may be any convex shaped model and is normally determined from the geometry of the molecule. The potential energy is written as a function of the minimum distance between molecular cores, which for the (6-12) intermolecular potential function is

$$U = U_o\left[\left(\frac{\rho_o}{\rho}\right)^{12} - 2\left(\frac{\rho_o}{\rho}\right)^{6}\right] \tag{35}$$

The second virial coefficient is then written as

$$\frac{B}{N_o} = \frac{2\pi}{3}\rho_o^3 F_3 + M_o\rho_o^2 F_2 + \left(S_o + \frac{M_o^2}{4\pi}\right)\rho_o F_1 + \left(V_o + \frac{M_o S_o}{4\pi}\right) \tag{36}$$

The functions F_1, F_2, and F_3 are functions of Z ($Z = U_o/kT$) and may be obtained from tabulated results* or calculated from the equation given by Kihara[54]

$$F_s = -\frac{s}{12}\sum_{t=o}^{\infty}\left[\frac{2^t}{t!}\Gamma\left(\frac{6t-s}{12}\right)\right]Z^{(6t+s)/12} \tag{37}$$

The parameters M_o, S_o, and V_o can be calculated directly from the size and shape of the core.

Prausnitz[69] has determined the parameters for the Kihara core model for a number of molecules including nitrogen. In addition he has taken into account the contribution of the quadrupole mement in nitrogen by assuming that the second virial coefficient is given by

$$B = B_{Kihara} + B_{quadrupole} \tag{38}$$

The value of the quadrupole contribution was calculated by Prausnitz from the relation of Pople,[68]

$$B_{quadrupole} = -\frac{2}{3}\pi N_o \sigma^3\left(\frac{7}{320}\right) Q^{*2} H_{10}(Z) \tag{39}$$

---

*The functions have been tabulated by Conolly[18] with Z as the argument from 0.01 to 7.0 in steps of 0.01.

where the dimensionless quantity Q^* is related the quadrupole moment Q by the relation

$$Q^* = \frac{Q^2}{U_o \sigma^5} \tag{40}$$

and σ is related approximately to ρ_o by the relation

$$\sigma = 2^{-1/6} \rho_o + \frac{M_o}{2\pi} \tag{41}$$

This relation is exact for spherical cores.

The function H_{10} is given by Pople[68] as

$$H_{10}(Z) = 2^{17/6} Z^{17/12} \sum_{p=0}^{\infty} \frac{2^p Z^{p/2}}{p!} \Gamma\left(\frac{6p+7}{12}\right) \tag{42}$$

Prausnitz[69] has obtained the following values of the various parameters for nitrogen assuming a spherocylindrical model for the core:

$M_o = 4.694$ Å, $S_o = 0.8130$ Å^2, $V_o = 0.03856$ Å^3

$\rho_o = 3.148$ Å, $U_o/k = 136.67$ °K, $Q^* = 0.2110$

3. Comparison of Experimental and Computed Second Virial Coefficients

A comparison of the experimental second virial coefficients of nitrogen below 200° K with the computed results is shown in Figure 8. Curve A was obtained using the Lennard-Jones (6-12) intermolecular potential function with the constants determined from the experimental data from Table XV. Curve B was calculated using the Kihara core model and the constants of Prausnitz.[69]

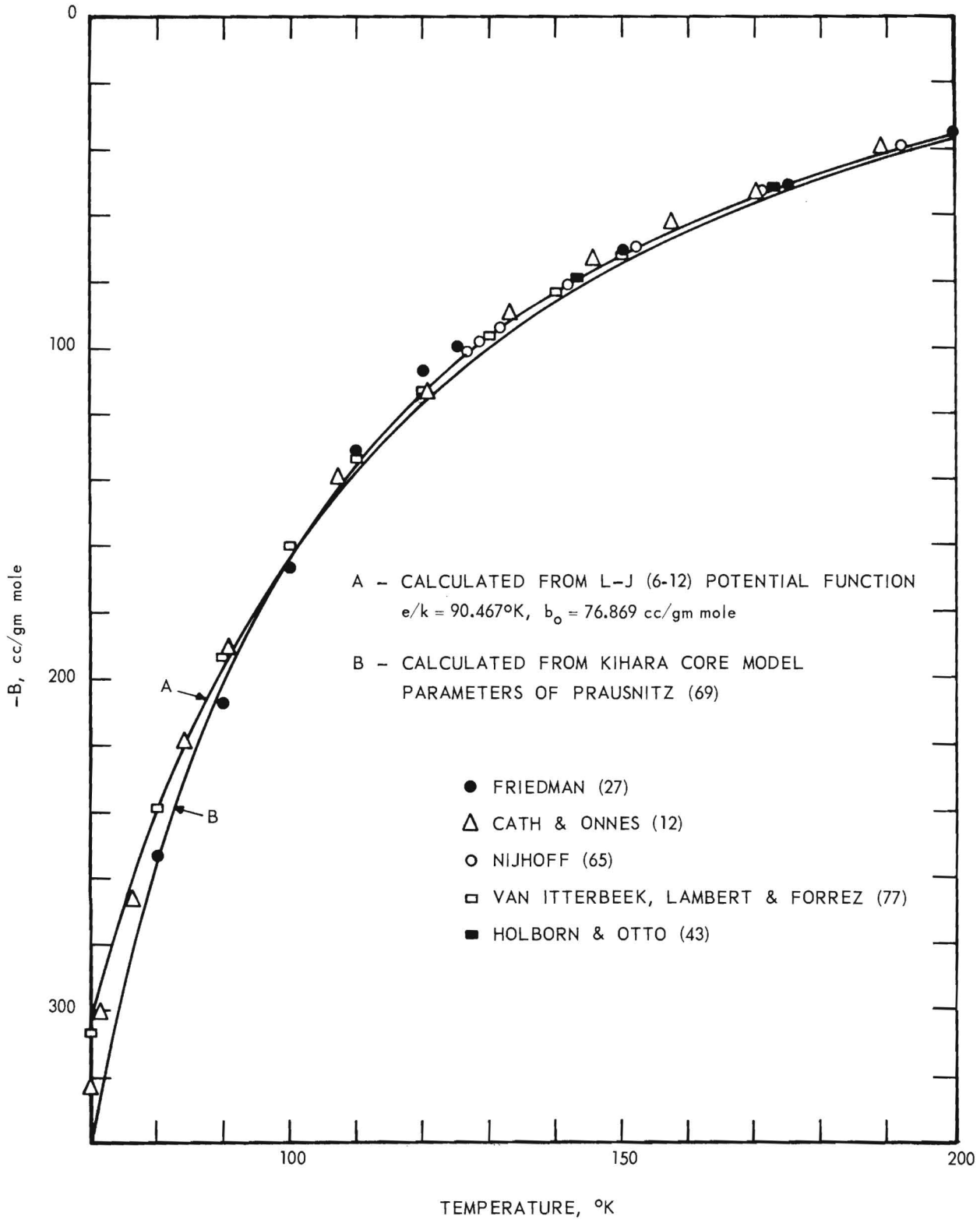

Figure 8. Second Virial Coefficient of Nitrogen.

D. Vapor Pressure and Heats of Vaporization and Sublimation of Nitrogen and Fluorine at One Degree Intervals

The results of the calculations for the vapor pressure and heats of vaporization and sublimation for nitrogen and fluorine are given in Tables XVI and XVII at one degree intervals from the normal boiling point down to 10° and 14° K, respectively. Also included for use in interpolation are the values $(1/T) \times 10^2$ and $\text{Log}_{10} P$ (P in mm Hg). The values for nitrogen given in Table XVI were computed using the input data listed in Table I. The values for fluorine given in Table XVII were computed using the input data given in Table IX.

TABLE XVI

VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF NITROGEN

Temperature, T (°K)	Pressure, P (mm Hg)	Heat of Vaporization (cal/gm mole)	$(1/T) \times 10^2$ ($°K^{-1}$)	Log P
77.347 (n.b.p.)	760.000	1334.8	1.29287	2.880814
77	729.398	1337.8	1.29870	2.862964
76	646.468	1346.2	1.31578	2.810547
75	570.972	1354.5	1.33333	2.756615
74	502.456	1362.6	1.35135	2.701098
73	440.479	1370.6	1.36986	2.643925
72	384.607	1378.4	1.38888	2.585017
71	334.420	1386.1	1.40845	2.524293
70	289.508	1393.7	1.42857	2.461661
69	249.482	1401.2	1.44927	2.397039
68	213.956	1408.5	1.47058	2.330324
67	182.563	1415.8	1.49253	2.261414
66	154.952	1422.9	1.51515	2.190198
65	130.785	1429.9	1.53846	2.116560
64	109.742	1436.9	1.56250	2.040376
63.152 (t.p.)	94.120	1442.7	1.58348	1.973680
- - - - - - - - - - - - - - - -		Solid		- - - - - - - - - - - - - -
63.152 (t.p.)	94.120	1615.0	1.58348	1.973680
63	91.221	1615.7	1.58730	1.960094
62	73.917	1620.5	1.61290	1.868745
61	59.472	1625.1	1.63934	1.774316
60	47.486	1629.5	1.66666	1.676562
59	37.614	1633.7	1.69491	1.575351
58	29.543	1637.7	1.72413	1.470461

(continued)

TABLE XVI(continued)

VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF NITROGEN

Temperature, T (°K)	Pressure, P (mm Hg)	Heat of Vaporization (cal/gm mole)	$(1/T) \times 10^2$ ($°K^{-1}$)	Log P
57	22.998	1641.6	1.75438	1.361697
56	17.697	1646.0	1.78571	1.247888
55	13.520	1649.5	1.81818	1.130963
54	10.220	1652.8	1.85185	1.009457
53	7.640	1656.1	1.88679	0.883100
52	5.645	1659.3	1.92307	0.751652
51	4.119	1662.4	1.96078	0.614762
50	2.966	1665.4	2.00000	0.472166
49	2.106	1668.4	2.04081	0.323459
48	1.473	1671.2	2.08333	0.168317
47	1.015	1674.0	2.12765	0.006277
46	6.870 (-1)	1676.6	2.17391	-0.163057
45	4.569 (-1)	1679.2	2.22222	-0.340211
44	2.981 (-1)	1681.7	2.27272	-0.525699
43	1.905 (-1)	1684.1	2.32558	-0.720083
42	1.191 (-1)	1686.4	2.38095	-0.924017
41	7.275 (-2)	1688.6	2.43902	-1.138177
40	4.332 (-2)	1690.7	2.50000	-1.363337
39	2.510 (-2)	1692.7	2.56410	-1.600339
38	1.412 (-2)	1694.7	2.63157	-1.850096
37	7.698 (-3)	1696.5	2.70270	-2.113649
36	4.054 (-3)	1698.2	2.77777	-2.392139
35.62 (tr.)	3.147 (-3)	1698.9	2.80741	-2.502140
35	2.028 (-3)	1756.1	2.85714	-2.692861
34	9.645 (-4)	1759.5	2.94117	-3.015699
33	4.378 (-4)	1762.4	3.03030	-3.358707
32	1.889 (-4)	1764.7	3.12500	-3.723677
31	7.715 (-5)	1766.5	3.22580	-4.112643
30	2.965 (-5)	1767.8	3.33333	-4.527922
29	1.066 (-5)	1768.8	3.44827	-4.972112
28	3.563 (-6)	1769.4	3.57142	-5.448238
27	1.097 (-6)	1769.6	3.70370	-5.959750
26	3.086 (-7)	1769.5	3.84615	-6.510623
25	7.844 (-8)	1769.0	4.00000	-7.105469
24	1.780 (-8)	1768.2	4.16666	-7.749662
23	3.552 (-9)	1767.1	4.34782	-8.449497
22	6.132 (-10)	1765.7	4.54545	-9.212408
21	8.970 (-11)	1763.9	4.76190	-10.047216
20	1.085 (-11)	1761.8	5.00000	-10.964494
19	1.054 (-12)	1759.3	5.26315	-11.977012

(continued)

TABLE XVI (concluded)

VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF NITROGEN

Temperature, T (°K)	Pressure, P (mm Hg)	Heat of Vaporization (cal/gm mole)	$(1/T) \times 10^2$ ($°K^{-1}$)	Log P
18	7.937 (-14)	1756.5	5.55555	-13.100343
17	4.429 (-15)	1753.4	5.88235	-14.353685
16	1.733 (-16)	1749.8	6.25000	-15.760991
15	4.441 (-18)	1745.9	6.66666	-17.352539
14	6.805 (-20)	1741.6	7.14285	-19.167192
13	5.550 (-22)	1737.0	7.69230	-21.255675
12	2.063 (-24)	1732.1	8.33333	-23.685515
11	2.827 (-27)	1726.8	9.09090	-26.548667
10	1.062 (-30)	1721.2	10.00000	-29.973674

TABLE XVII

VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF FLUORINE

Temperature, T (°K)	Pressure, P (mm Hg)	Heat of Vaporization (cal/gm mole)	$(1/T) \times 10^2$ ($°K^{-1}$)	Log P
85.03 (n.b.p.)	760.000	1561.3	1.17606	2.880814
85	757.397	1561.6	1.17647	2.879323
84	674.664	1570.5	1.19047	2.829088
83	599.186	1579.3	1.20481	2.777561
82	530.506	1587.9	1.21951	2.724690
81	468.182	1596.3	1.23456	2.670414
80	411.790	1604.6	1.25000	2.614676
79	360.919	1612.7	1.26582	2.557410
78	315.174	1620.7	1.28205	2.498550
77	274.171	1628.6	1.29870	2.438022
76	237.552	1636.3	1.31578	2.375760
75	204.966	1644.0	1.33333	2.311681
74	176.077	1651.5	1.35135	2.245702
73	150.569	1658.9	1.36986	2.177737
72	128.142	1666.3	1.38888	2.107693
71	108.511	1673.5	1.40845	2.035473
70	91.406	1680.7	1.42857	1.960976
69	76.576	1687.9	1.44927	1.884091
68	63.783	1694.9	1.47058	1.804703
67	52.807	1702.0	1.49253	1.722691
66	43.444	1708.9	1.51515	1.637925

(continued)

TABLE XVII (continued)

VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF FLUORINE

Temperature, T (°K)	Pressure, P (mm Hg)	Heat of Vaporization (cal/gm mole)	$(1/T) \times 10^2$ ($°K^{-1}$)	Log P
65	35.503	1715.9	1.53846	1.550266
64	28.812	1722.8	1.56250	1.459569
63	23.210	1729.7	1.58730	1.365673
62	18.507	1737.4	1.61290	1.267332
61	14.680	1744.1	1.63934	1.166728
60	11.544	1750.8	1.66666	1.062373
59	8.996	1757.6	1.69491	0.954069
58	6.944	1764.3	1.72413	0.841602
57	5.306	1771.1	1.75438	0.724743
56	4.011	1777.9	1.78571	0.603247
55	2.998	1784.7	1.81818	0.467851
54	2.214	1791.6	1.85185	0.345271
53.54 (t.p.)	1.918	1794.8	1.86776	0.282918
- - - - - - - - - - - - - - - - - -		Solid	- - - - - - - - - -	
53.54 (t.p.)	1.918	1916.7	1.86776	0.282918
53	1.596	1919.6	1.88679	0.203146
52	1.124	1924.7	1.92307	0.050726
51	7.797 (-1)	1929.7	1.96078	-0.108090
50	5.325 (-1)	1934.6	2.00000	-0.273685
49	3.577 (-1)	1939.4	2.04081	-0.446470
48	2.361 (-1)	1944.0	2.08333	-0.626890
47	1.530 (-1)	1948.5	2.12765	-0.815429
46	9.714 (-2)	1952.8	2.17391	-1.012612
45.55 (tr.)	7.865 (-2)	1954.7	2.19538	-1.104312
45	5.899 (-2)	2130.6	2.22222	-1.229185
44	3.431 (-2)	2134.0	2.27272	-1.464550
43	1.944 (-2)	2137.0	2.32558	-1.711212
42	1.072 (-2)	2139.6	2.38095	-1.969968
41	5.733 (-3)	2141.9	2.43902	-2.241645
40	2.970 (-3)	2143.8	2.50000	-2.527194
39	1.487 (-3)	2145.5	2.56410	-2.827647
38	7.176 (-4)	2146.8	2.63157	-3.144126
37	3.327 (-4)	2147.9	2.70270	-3.477909
36	1.478 (-4)	2148.8	2.77777	-3.830390
35	6.264 (-5)	2149.3	2.85714	-4.203127
34	2.524 (-5)	2149.6	2.94117	-4.597873
33	9.626 (-6)	2149.6	3.03030	-5.016571
32	3.456 (-6)	2149.4	3.12500	-5.461411
31	1.162 (-6)	2148.9	3.22580	-5.934868
30	3.633 (-7)	2148.1	3.33333	-6.439743
29	1.049 (-7)	2147.0	3.44827	-6.979199
28	2.774 (-8)	2145.7	3.57142	-7.556869
27	6.654 (-9)	2144.1	3.70370	-8.176906

(continued)

TABLE XVII (concluded)

VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF FLUORINE

Temperature, T (°K)	Pressure, P (mm Hg)	Heat of Vaporization (cal/gm mole)	$(1/T) \times 10^2$ ($°K^{-1}$)	Log P
26	1.432 (-9)	2142.2	3.84615	-8.844093
25	2.729 (-10)	2140.0	4.00000	-9.563969
24	4.540 (-11)	2137.5	4.16666	-10.342985
23	6.476 (-12)	2134.8	4.34782	-11.188703
22	7.762 (-13)	2131.7	4.54545	-12.110042
21	7.628 (-14)	2128.3	4.76190	-13.117604
20	5.969 (-15)	2124.7	5.00000	-14.224092
19	3.590 (-16)	2120.7	5.26315	-15.444858
18	1.590 (-17)	2116.5	5.55555	-16.798641
17	4.914 (-19)	2111.9	5.88235	-18.308551
16	9.921 (-21)	2107.1	6.25000	-20.003446
15	1.203 (-22)	2102.1	6.66666	-21.919823
14	7.860 (-25)	2096.8	7.14285	-24.104557

TECHNICAL REPORT NO. 2

PROJECT NO. A-663

CALCULATION OF THE VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF LIQUIDS AND SOLIDS, ESPECIALLY BELOW ONE ATMOSPHERE. V. CARBON MONOXIDE AND CARBON DIOXIDE

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ABSTRACT

The vapor pressure and heats of vaporization and sublimation of carbon monoxide have been computed at one degree intervals from the normal boiling point (81.638° K) to 14° K. The vapor pressure and heats of sublimation of carbon dioxide have been computed at one degree intervals from the normal sublimation temperature (194.694° K) to 40° K.

The agreement obtained between the computed and experimental vapor pressure data for carbon monoxide in the liquid and solid region down to the solid transition point (61.544° K) suggests that the computed values may well represent the experimental data within the accuracy of the temperature scales used by the various investigators. The computed values of the vapor pressures (Table XIX) are therefore recommended for use as smoothed values, especially below the solid transition temperature where the limited experimental data are scattered and discordant.

For carbon dioxide the computed values of the vapor pressures agree well with the best experimental data which have been obtained on the thermodynamic scale. The experimental data measured on the International Temperature Scale appeared to deviate in a manner which is consistent with the available known deviations of the International Temperature Scale from the thermodynamic scale. The values of the vapor pressure of carbon dioxide computed at one degree intervals (Table XX) are therefore recommended as a consistent set of values on the thermodynamic temperature scale.

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I. INTRODUCTION

In a previous report[82] a number of thermodynamic relations were presented for the calculation of the vapor pressure and heats of vaporization and sublimation of liquids and solids. These thermodynamic relations are similar in principle to relations developed by other investigators.[29, 28, 73, 23, 69] These relations have been used to compute the vapor pressures and heats of vaporization and sublimation of ethylene,[82] oxygen,[61] argon,[84] methane,[85] parahydrogen,[60] nitrogen,[83] and fluorine[83] from approximately their normal boiling point to or below 20° K. In the case of parahydrogen the calculations were made to 1° K.

The present report is concerned with the application of the thermodynamic relations previously developed[82] to carbon monoxide and carbon dioxide. The principal thermodynamic relations used are summarized in the next section. The necessary available thermodynamic data have been used to compute the vapor pressure of carbon monoxide and carbon dioxide, the heats of vaporization and sublimation of carbon monoxide, and the heats of sublimation of carbon dioxide from their normal boiling or sublimation point to 14° K and 40° K respectively. The computed results have been compared with experimental vapor pressure and heat of vaporization or sublimation data where available.

II. THERMODYNAMIC RELATIONS

A. Variation of Heat of Vaporization and Sublimation with Temperature

By performing an enthalpy cycle between two points, (P,T) and (P_1,T_1), on the vapor pressure curve of a pure substance it can be shown[82] that the heat of vaporization or sublimation at the temperature T_1 can be computed from Equation (1).*

$$(\Delta H_v)_T = (\Delta H_v)_{T_1} + \int_T^{T_1} c_s' \, dT + \sum_T^{T_1} (\Delta H_{tr})' - \left[(H^o - H_o^o)_{T_1}'' - (H^o - H_o^o)_T'' \right] - RT_1 \delta_1 + RT\delta + \int_P^{P_1} v_s' \, dP \qquad (1)$$

In this equation the quantity δ is given by the relation

$$RT\delta = [H(P,T) - H^o(T)]'' \qquad (2)$$

and δ_1 is the value of δ at the point (P_1, T_1). The prime (') and double prime (") symbols refer to the condensed and vapor phases, respectively. The evaluation of the right-hand side of Equation (2) requires an equation of state for the vapor. If a virial form of the equation of state is used, namely,

$$PV = RT\left(1 + \frac{B}{V}\right) \qquad (3)$$

where the second virial coefficient, B, is assumed to be a function of temperature only, then one obtains

$$\delta = \left(B - T\frac{dB}{dT}\right)/V \qquad (4)$$

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*All symbols are defined in Appendix A.

For temperatures below the triple point, $(\Delta H_v)_T$ in Equation (1) is the heat of sublimation rather than the heat of vaporization. The evaluation of the last two terms of Equation (1) requires a value of the vapor pressure at T. If vapor pressure calculations are made by an iterative procedure, then this iterative procedure also provides the pressure necessary to compute the last two terms of Equation (1).

B. Vapor Pressure Relations

From a known point (P_1,T_1) on the vapor pressure curve, the vapor pressure at any other point (P,T) can be calculated from the previously derived relation[82]

$$\ln P = \ln P_1 - (\Delta H_v)_{T_1}(T_1 - T)/RTT_1 + \left[(H^o - H_o^o)''_{T_1} - (H^o - H_o^o)''_T\right]/RT$$

$$- \left[(S^o)''_{T_1} - (S^o)''_T\right]/R - \left(\int_T^{T_1} c_s' \, dT\right)/RT - \left(\sum_T^{T_1} (\Delta H_{tr})'\right)/RT$$

$$+ \left(\int_T^{T_1} c_s' \, dT/T\right)/R + \left(\sum_T^{T_1} (\Delta H_{tr})'/T_{tr}\right)/R + \delta_1(T_1 - T)/T$$

$$- \varepsilon_1 + \varepsilon - \left(\int_P^{P_1} v_s' \, dP\right)/RT \qquad (5)$$

where

$$\varepsilon = \left[H^o(T) - H(P,T)\right]''/RT - \left[S^o(P,T) - S(P,T)\right]''/R \qquad (6)$$

and ε_1 is the value of ε at (P_1,T_1). If the virial form of the equation of state is assumed, i.e., Equation (3), then ε becomes

$$\varepsilon = \ln (PV/RT) - 2B/V \qquad (7)$$

Equation (5), which may be considered to be an integration of the Clapeyron equation, can be solved if appropriate thermal data for the condensed phase; $(\Delta H_v)_{T_1}$ at (P,T_1); an equation of state for the real gas; and the requisite molecular structure data for the ideal gas are available. Solution of Equation (5) requires iteration since the last two terms are pressure dependent.

III. VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF CARBON MONOXIDE

A. Introduction

The vapor pressure and heats of vaporization and sublimation of carbon monoxide have been calculated from its normal boiling point, 81.638° K, to 14° K using the appropriate equations from Section II and selected values for its physical properties. These calculated vapor pressures have been compared with the available experimental values. In addition, a comparison of the entropies calculated from calorimetric data and from statistical mechanical methods has been made at the normal boiling point.

B. Review of Experimental Data for Carbon Monoxide

1. General

The calculation of vapor pressures from Equation (5) and heats of vaporization and sublimation from Equation (1) for carbon monoxide in the temperature range from the normal boiling point, T_1, to 14° K requires the following data: the temperature of and the heat of vaporization at the normal boiling point; all heats of condensed phase transitions and the temperatures at which these transitions occur; and the saturated heat capacity and molal volume of the condensed phase over the entire temperature range. A representation of the second virial coefficient as a function of temperature is also required. The effect of higher virial coefficients is assumed to be negligible at pressures below one atmosphere. In addition, molecular structure data are required to permit the calculation of the thermodynamic properties of the ideal gas.

From a survey of the literature, a selection has been made of the "best" values of these thermal and related properties of carbon monoxide. These

selected values are summarized in Table I. The reasons for these selections together with a review of the more recent data are discussed in the following sections. Some of the older data are not included in these discussions since they are included in a recent review by Leah.[47] The temperatures of all transition points and vapor pressure data have been corrected, wherever possible, to a thermodynamic temperature scale having an assigned ice point of 273.15° K. A further discussion of this scale and the methods of temperature correction used are given in Appendix B. No temperature corrections have been applied to heat capacity, molal volume of the condensed phases, or second virial coefficient data since such corrections are believed to be smaller than the experimental error of these data. For the same reason, no corrections have been applied to energy quantities to bring them to a uniform base; however, all calculations have been made on the basis of the defined calorie (1 defined calorie = 4.1840 ab. joules = 4.1833 int. joules).

2. Normal Boiling Point of Carbon Monoxide

The normal boiling points of carbon monoxide which have been reported to a precision of greater than 0.1° K are summarized in Table II. The value attributed to Von Winning is that corrected value quoted by Clusius and Teske.[11] The value attributed to Clusius and Teske is that obtained by them by extrapolating their measured vapor pressures upward from their highest temperature of 79.967° K by a thermodynamic method similar to the methods used in this work. The other values are those obtained by the particular investigators by interpolation of their vapor pressures measured at temperatures near the normal boiling point.

TABLE I

SELECTED PHYSICAL PROPERTIES OF CARBON MONOXIDE

Property	Selected Value	Table No.
Normal boiling point (nbp)	81.638° K	II
Triple point temperature	68.127° K	III
Solid transition temperature	61.544° K	IV
Heat of vaporization (nbp)	1443.6 cal/gm mole	V
Heat of fusion	200.7 cal/gm mole	V
Heat of solid transition	151.2 cal/gm mole	V
Heat capacity of condensed phases	Equation (8)	VI
Mean molal volume of condensed phases	--	VI
Second virial coefficient		Appendix C
Lennard-Jones (6-12) parameters		
ϵ/k	100.12° K	
b_o	67.60 cc/gm mole	
Molecular parameters	--	VII
Molecular weight	28.011	

The correction of the temperature reported by Heuse and Otto[36] has been made on the basis of their reported oxygen boiling point (90.195° K) rather than their ice point (273.16° K); this is similar to our previous treatments of temperature scales which use both points as defined points, and results in better agreement with other investigators.

The selected value for the normal boiling point represents an arithmetic average of the last five entries in Table II.

TABLE II

NORMAL BOILING POINT OF CARBON MONOXIDE

Reported Temperature (°K)	Method of Correction[a]	Corrected Temperature (°K)	Investigator	Year
81.66	16	81.678	Von Winning[11]	1919
81.62	16	81.638	Clusius & Teske[11]	1929
81.619	16	81.636	Crommelin et al[18]	1931
81.62	16	81.638	Verschoyle[77]	1931
81.61	16	81.628	Clayton & Giauque[8]	1932
81.676	20	81.652	Heuse & Otto[36]	1932
Selected Value		81.638		

[a]Entries refer to equations in Appendix B.

3. Triple Point of Carbon Monoxide

The more recent determinations of the triple point of carbon monoxide are summarized in Table III. There appears to be considerable disagreement in these values. A similar review of the triple point data has been made by Clusius et al[12] who assign an uncertainty of 0.05° K to the triple point temperature.

The temperature reported by Clusius and Teske[11] was measured with nitrogen and oxygen vapor pressure thermometers using the data of Cath[7] to relate the observed pressures to temperatures. Those reported by Crommelin et al[18] and Verscholye[77] were determined using platinum resistance thermometers. The temperature given by Clayton and Giauque[8] was determined by thermocouple thermometry

based on a gas thermometer calibration. The value reported by Kaischev[48] was measured with a platinum resistance thermometer; however, no details concerning its calibration were given. The more recent value of Clusius et al[12] was determined by nitrogen vapor pressure thermometry based on the nitrogen vapor pressure relation of Giauque and Clayton.[24]

TABLE III

TRIPLE POINT OF CARBON MONOXIDE

Reported Temperature (°K)	Method of Correction[a]	Corrected Temperature (°K)	Reported Pressure (mm Hg)	Year	Investigator
67.3	--	--	--	1916	Eucken[20]
68.20[b]	--	--	--	1923	Physikalisch Tech. Reichsanstalt
68.22	16	68.235	--	1929	Clusius & Teske[11]
68.10	16	68.115	115.11	1931	Crommelin et al[18]
68.09	16	68.105	115.30	1932	Clayton & Giauque[8]
68.06	16	68.075	114.86	1931	Verschoyle[77]
68.10	--	--	115.4	1938	Kaischev[42]
--	--	--	115.38	1941	Clusius & Stavely[10]
--	--	--	115.44	1956	Mathot et al[54]
68.15	15	68.162	115.3	1960	Clusius et al[12]
	Selected Value	68.127			

[a] Entries refer to equations in Appendix B.

[b] Quoted by Clusius et al[12]

The selected value for the triple point temperature of carbon monoxide is the arithmetic average of the corrected values of Crommelin et al, Clusius et al, and Clayton and Giauque.

4. Solid Phase Transition Temperature of Carbon Monoxide

As is the case with nitrogen, carbon monoxide has two stable solid phases, the lower temperature modification being designated alpha-solid and the higher temperature one, beta-solid. The alpha-beta solid phase transition temperatures which have been reported are summarized in Table IV.

The selected value represents the average of the values of Clusius, and Clayton and Giauque.

TABLE IV

SOLID TRANSITION TEMPERATURE OF CARBON MONOXIDE

Reported Temperature (°K)	Method of Correction[a]	Corrected Temperature (°K)	Year	Investigator
60.4	--	--	1916	Eucken[20]
61.51	16	61.524	1929	Clusius[9]
61.55	16	61.564	1932	Clayton & Giauque[8]
61.49	--	--	1938	Kaischev[42]
	Selected Value	61.544		

[a]Entries refer to equations in Appendix B.

5. Heats of Transition of Carbon Monoxide

a. Heat of Vaporization. The two reported calorimetric determinations of the heat of vaporization of carbon monoxide at the normal boiling

point are shown in Table V. The value reported by Eucken has not been used since his higher temperature calorimetric data are not in good agreement with the results of other investigators. The selected value is, therefore, that reported by Clayton and Giauque.

b. Heat of Fusion. The reported heats of fusion of carbon monoxide are summarized in Table V. The selected value was taken as the arithmetic average of the last three values listed.

c. Heat of Alpha-Beta Solid Phase Transition. The reported heats of the alpha-beta solid phase transition of carbon monoxide are summarized in Table V. With the exception of the value reported by Eucken, these data are in very good agreement. The selected value is taken as the arithmetic average of the last three entries of Table V.

6. Heat Capacities of Condensed Carbon Monoxide

a. General. Heat capacities for the condensed phases of carbon monoxide have been reported by Eucken[20] from 17.5° to 65.6° K, by Clusius[9] from 11.89° to 81.3° K, by Clayton and Giauque[8] from 14.36° to 84.66° K, and by Kaischev[42] from 54.22° to 75.81° K. All of the reported values are assumed to be saturated heat capacities rather than constant pressure heat capacities. For calculational purposes, these data were represented by temperature polynomials of the form shown in Equation (8), the coefficients of which were determined by a least-squares procedure. These coefficients are shown in Table VI.

$$c_s' = A_0 + A_1T + A_2T^2 + A_3T^3 + A_4T^4 + A_5T^5 \qquad (8)$$

TABLE V

HEATS OF TRANSITION OF CARBON MONOXIDE

Heat of Transition (cal/gm mole)		Investigator	Year
Heat of Vaporization at nbp			
1414		Eucken[20]	1916
1443.6		Clayton & Giauque[8]	1932
1443.6	Selected Value		
Heat of Fusion			
198.2[a]		Eucken	1916
201.5		Clusius[9]	1929
199.7		Clayton & Giauque[8]	1932
200.9		Kaischev[42]	1938
200.7	Selected Value		
Heat of Alpha-Beta Solid Transition			
144.1		Eucken[20]	1916
151.2		Clusius[9]	1929
151.3_5		Clayton & Giauque[8]	1932
150.9		Kaischev[42]	1938
151.2	Selected Value		

[a]Corrected value given by Clusius[9]

TABLE VI

COEFFICIENTS FOR HEAT CAPACITY POLYNOMIALS
AND MEAN MOLAL VOLUMES FOR LIQUID AND SOLID CARBON MONOXIDE

			Alpha-Solid		
				Below 44° K	
	Liquid	Beta-Solid	Above 44° K	Data of Clayton & Giauque[8]	Data of Clusius[9] and Eucken[20]
A_0	14.44	7.1621621	0.0	0.0	0.0
A_1	0.0	0.0775629	-1.0469298	-0.47423848	0.059584621
$A_2 \times 10^2$	0.0	0.0	7.9050935	7.7120104	-0.1224473
$A_3 \times 10^3$	0.0	0.0	-1.6720370	-3.3634578	0.69280833
$A_4 \times 10^5$	0.0	0.0	1.1854107	6.5626308	-2.2922599
$A_5 \times 10^7$	0.0	0.0	0.0	-4.7845560	2.1622803
Minimum Temperature, ° K	68.127	61.544	44.00	14.36	11.89
Maximum Temperature, ° K	84.66	68.127	61.544	44.00	44.00
Mean Molal Volume, Liters/gm mole	0.03430	0.03015	0.02723	0.02723	0.02723

b. Liquid Range. The heat capacity data for liquid carbon monoxide between its triple point and normal boiling point are reasonably consistent. In view of the small, more-or-less random error in all of the data, the liquid phase heat capacity has been taken to be a constant value obtained from the arithmetic average of the nine heat capacities reported by Clayton and Giauque.

c. Beta-Solid Range. The heat capacities for beta-solid carbon monoxide reported by Eucken are not in good agreement with the data of the

other investigators. The data of Clusius, Clayton and Giauque, and Kaischev were fitted to a linear temperature function by a least-squares procedure in which c_s' was taken as the dependent variable.

d. Alpha-Solid Range. In the temperature range from about 44° K to the alpha-beta transition (61.544° K), the heat capacity data are, with the exception of those of Eucken, in reasonably good agreement. For this temperature range, the data of Clusius, Clayton and Giauque, and Kaischev were fitted by a least-squares procedure in which the dependent variable was taken as c_s'/T.

Below about 44° K, the data of Eucken are in reasonable agreement with those of Clusius; both are, however, in considerable disagreement with the data of Clayton and Giauque. This disagreement becomes quite apparent upon examination of a graph of c_s'/T vs T. Since there is no a priori reason to prefer one set of data more than the other, polynomials were fitted separately to the combined Eucken and Clusius data and to the data of Clayton and Giauque by a least-squares procedure in which c_s'/T was used as the dependent variable. A good joining of the low and high temperature polynomial representations of the heat capacities of alpha-solid carbon monoxide was obtained by giving triple weight to the two data points of Clayton and Giauque and the one of Clusius in the vicinity of 44.5° K.

7. Molal Volumes of Condensed Carbon Monoxide

a. Liquid Phase. Baly and Donnan[4] have measured the densities of liquid carbon monoxide from 70.96° to 87.69° K. Mathias and Crommelin[52] have measured densities from 68.13° to 131.39° K. Mathot et al[54] have reported the liquid density at 90.67° K. These data were converted to molal volumes and graphed. It was found that the point of Mathot et al agrees well with the data

of Mathias and Crommelin, and that the data of Baly and Donnan were slightly lower.

The selected mean value of the molal volume of liquid carbon monoxide for the temperature range between its triple point and normal boiling point was taken to be 34.30 ml/gm mole, a value which corresponds to a vapor pressure of one-half atmosphere.

b. Beta-Solid Phase. By applying the Clapeyron equation, Clusius et al[12] have used their measured melting curve for carbon monoxide to calculate the change of molal volume upon freezing. On the basis of the measured liquid density of Mathias and Crommelin, they deduced the value 30.318 cc/gm mole for the molal volume of saturated beta-solid carbon monoxide at its triple point. In addition, Vegard[76] has determined the density of the beta-solid at 65° K from X-ray diffraction data. His density corresponds to a molal volume of 30.15 ml/gm mole. Since this value of Vegard lies about midway of the stable temperature range of the beta-solid phase, it was selected.

c. Alpha-Solid Phase. The only determination of the density of the alpha-solid phase of carbon monoxide which has been reported is that determined at 20° K from X-ray diffraction data by Vegard.[76] His value corresponds to a molal volume of 27.23 ml/gm mole. In the absence of other data, this value was selected.

8. Second Virial Coefficient of Carbon Monoxide

Detailed discussions of the available experimental values for the second virial coefficient of carbon monoxide and the analytical representation of these data are given in Appendix C.

While the Kihara core model is in better agreement with the limited experimental data, it was found that the Lennard-Jones model produced a markedly better fit to the experimental vapor pressure data when combined with the other selected values for the physical properties of carbon monoxide. A further discussion of this matter is given below.

9. Molecular Parameters of Carbon Monoxide

The molecular parameters for carbon monoxide have been very precisely measured by both optical and microwave techniques; indeed, the rotational constants have been used by Rank et al[66] and Plyler et al[63] as a method of determining the velocity of light. Further, Rosenblum et al[67] have used their microwave determinations of the rotational constants for the various isotopic species of carbon monoxide to accurately calculate the relative masses of the several carbon and oxygen isotopes.

Benedict et al[5] have recently presented complete sets of the molecular parameters for all of the stable isotopic species of carbon monoxide and the natural abundance ratios of these species. These values are in excellent agreement with other recent values and have been selected for calculating the ideal gas thermodynamic properties of carbon monoxide in this work. The values of the molecular parameters applying to the rigid-rotator, harmonic-oscillator molecular model and the percentage natural abundance for the six stable isotopic species are shown in Table VII together with values representing the average for the four less abundant isotopic species. The rotational constant, B_o, was determined from the quoted values of B_e and α_e, and the vibrational wave number, ω, from the quoted values of ω_e and $x_e\omega_e$ using the conversions recommended by Mayer and Mayer.[55]

The molecular weight of carbon monoxide, 28.011 on the chemical scale, was taken from Wichers.[80]

TABLE VII

MOLECULAR PARAMETERS FOR CARBON MONOXIDE

Isotopic Species	Percent Abundance	B_o (cm^{-1})	ω (cm^{-1})
$C^{12}O^{16}$	98.654	1.92265	2143.236
$C^{13}O^{16}$	1.106	1.83807	2116.040
$C^{12}O^{18}$	0.202	1.83178	2092.089
$C^{12}O^{17}$	0.037	1.87407	2116.261
$C^{13}O^{18}$	0.00226	1.73750	2043.668
$C^{13}O^{17}$	0.00041	1.78949	2068.426
$(CO)^a$	0.240[b]	1.83729	2095.289

[a] These constants represent the concentration weighted average for the species $C^{12}O^{18}$, $C^{12}O^{17}$, $C^{13}O^{18}$, and $C^{13}O^{17}$.

[b] The actual sum is 0.242. This was adjusted to make the total sum over all the isotopic species 100 percent.

10. Experimental Vapor Pressures of Carbon Monoxide

In order to assess the accuracy of the calculated vapor pressures, experimental vapor pressures are needed. Clusius and Teske[11] have measured the vapor pressure of carbon monoxide from 60.34° to 79.97° K using both oxygen

and nitrogen vapor pressure thermometers. The temperature scale was determined by using the oxygen and nitrogen vapor pressure data of Cath.[7] Heuse and Otto[36] measured vapor pressures in the immediate vicinity of the normal boiling point for carbon monoxide using a helium-filled gas thermometer. Verschoyle[77] and Crommelin et al[18] have made such measurements from well above the normal boiling point down to 54.21° and 56.86° K, respectively; both used platinum resistance thermometers calibrated on the temperature scale of the University of Leiden. Clayton and Giauque[8] measured carbon monoxide vapor pressures from 60.24° to 83.13° K using a thermocouple thermometer which had been calibrated against a hydrogen-filled gas thermometer to which the corrections recommended by Cath and Kammerlingh-Onnes of the University of Leiden were applied.

It appears, then, with the exception of the limited data of Heuse and Otto, that all of the experimental vapor pressures have been determined using thermometer calibrations which are traceable to the temperature scale of the University of Leiden.

C. Computational Methods

1. General

The numerical solutions of Equations (5) and (1) for the vapor pressure and heats of vaporization and sublimation of carbon monoxide were made at one degree intervals from the normal boiling point down to 14° K using an automatic digital computer.

A constant mean value of the molal volume of the condensed phase was assumed to apply over the temperature range of each heat capacity polynomial. The methods employed to compute the values of the second virial coefficient are described in Appendix C. The gas nonideality corrections were applied down to

the point where these corrections changed the calculated vapor pressure by less than 0.001 percent.

The comparison of the experimental with the calculated vapor pressures involves interpolation (and occasionally slight extrapolation) in the table of calculated values. This was accomplished by using Aitken's method of polynomial interpolation as described by Milne.[59]

2. Calculation of Ideal Gas Thermodynamic Properties

The ideal gas thermodynamic properties of carbon monoxide were calculated using the rigid-rotator, harmonic-oscillator model. The relations used are those of Mayer and Mayer.[55]

$$\frac{(H^o - H_o^o)}{RT} = \frac{5}{2} + \frac{x}{e^x - 1} + 1 - \frac{y}{3} - \frac{y^2}{45} - \frac{8y^3}{945} \qquad (9)$$

$$\frac{S^o}{R} = \frac{5}{2} \ln T + \frac{3}{2} \ln M - 1.164862 + \frac{x}{e^x - 1}$$

$$- \ln(1 - e^{-x}) + 1 - \ln y - \frac{y^2}{90} - \frac{16y^3}{2835} \qquad (10)$$

In these two equations, $x = hc\omega/kT$ and $y = hcB_o/kT$.

Lewis et al[48] present relations for correcting the rigid-rotator, harmonic-oscillator calculations to the more accurate (first order corrections) anharmonic-oscillator calculations. Utilizing these relations together with the molecular parameters of Benedict et al,[5] it was determined that these corrections are negligible in the temperature range of these vapor pressure computations.

The properties for the natural isotopic mixture of carbon monoxide were calculated by making separate calculations using the molecular parameters for

the species $C^{12}O^{16}$ and $C^{13}O^{16}$ and also using the single set of concentration weighted average parameters for the remaining four species which are shown in Table VII. The properties of the normal isotopic species were then taken as the concentration weighted average of the properties of these three "species." The entropy of isotopic mixing is, therefore, not included in this calculated value.

D. Discussion of Results

1. Results of Calculations

Two questions concerning the properties of carbon monoxide were not resolved from the survey of the published data. First, no selection was made between the two heat capacity polynomials for the alpha-solid phase below 44° K. Second, no final selection was made between the Lennard-Jones (6-12) model and the Kihara core model for representing the second virial coefficient of carbon monoxide, although the Kihara core model used with the parameters given by Prausnitz and Myers[65] is in good agreement with the single, low temperature, experimental value by Mathot et al.[54]

For purposes of comparing the effects of the heat capacity polynomials, the second virial coefficient representation has negligible effects below 44° K. The equivalent temperature differences introduced into the calculated values of the vapor pressure below 44° K by the use of the heat capacity polynomial fitted to the combined data of Clusius and Eucken rather than the polynomial fitted to the data of Clayton and Giauque are shown in Figure 1. The direct comparison of these calculated vapor pressures is shown in Table VIII. These differences are quite small and are not resolvable on the basis of the available experimental data. The polynomial fitted to the data of Clayton and Giauque was selected for use in all further calculations below 44° K.

TABLE VIII

COMPARISON OF CALCULATED VAPOR PRESSURES
USING DIFFERENT SECOND VIRIAL COEFFICIENT REPRESENTATIONS
AND DIFFERENT LOW TEMPERATURE SOLID HEAT CAPACITIES

Temperature (°K)	Calculated Vapor Pressure (mm Hg)		
	LJ[a]	K[b]	CE[c]
80.000	6.2800 (2)[d]	6.2726 (2)	--
70.000	1.5752 (2)	1.5624 (2)	--
68.127	1.1551 (2)	1.1443 (2)	--
65.000	6.1306 (1)	6.0596 (1)	--
61.544	2.8089 (1)	2.7695 (1)	--
55.000	4.1132 (0)	4.0324 (0)	--
50.000	6.5855 (-1)	6.4335 (-1)	--
44.000	4.1159 (-2)	3.9958 (-2)	4.1159 (-2)
40.000	4.0338 (-3)	3.8959 (-3)	4.0338 (-3)
30.000	7.8990 (-7)	7.4857 (-7)	7.8673 (-7)
20.000	3.3559 (-14)	3.0619 (-14)	3.2844 (-14)

[a]Calculated from selected values of Table I using the Lennard-Jones (6-12) model for the second virial coefficient and the heat capacity polynomial fitted to the data of Clayton and Giauque below 44° K.

[b]Same as a except using the Kihara core model and the parameters of Prausnitz and Meyers for the second virial coefficient.

[c]Same as a except using the heat capacity polynomial fitted to the combined data of Clusius and Eucken below 44° K.

[d]Numbers in parentheses indicate powers of ten by which the entry is to be multiplied.

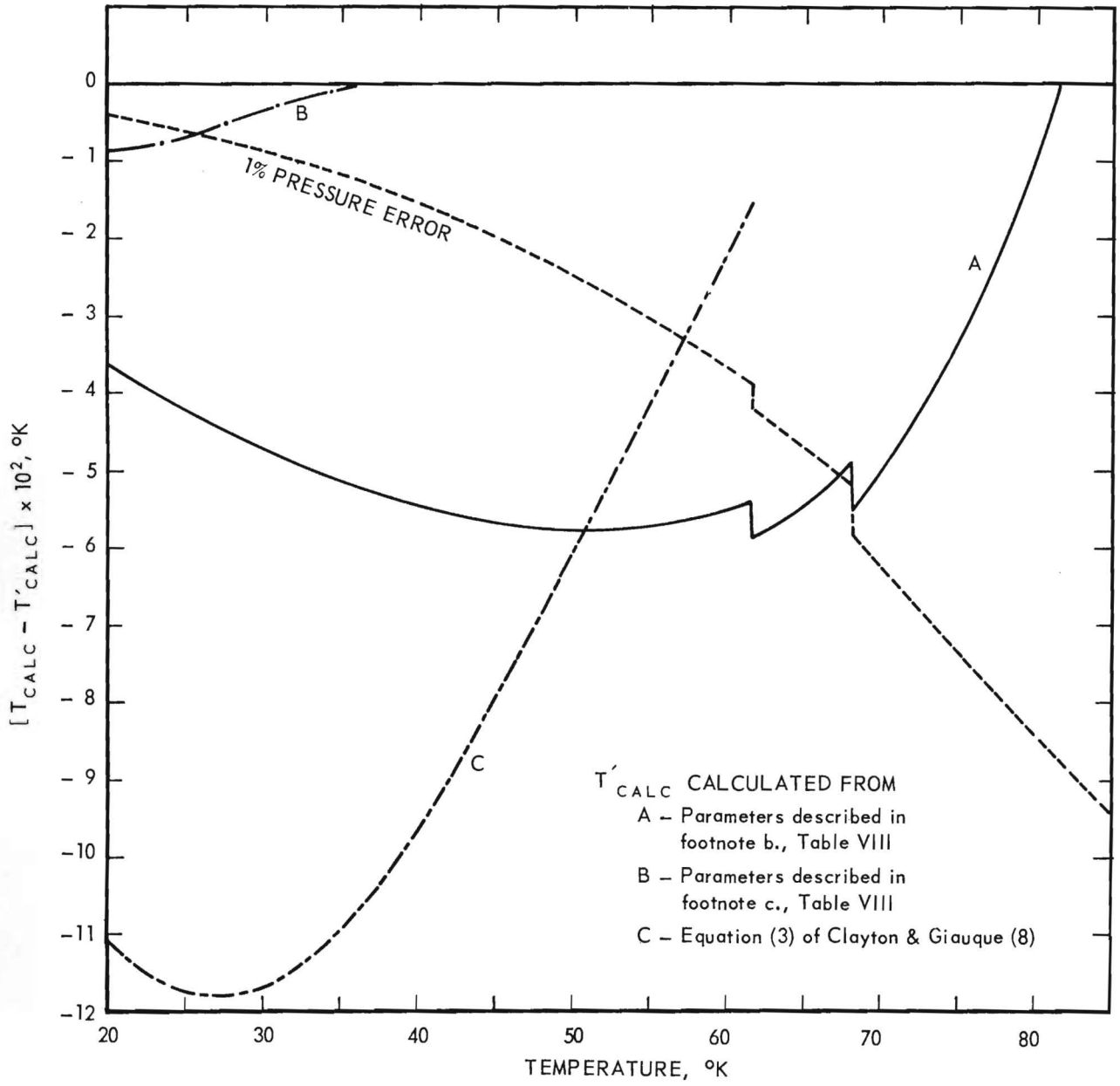

Figure 1. Comparison of Calculated Vapor Pressures with Selected Calculated Vapor Pressures (Table XIX) of Carbon Monoxide.

The vapor pressure of carbon monoxide was calculated at one degree intervals from the normal boiling point to 14° K using each of the two representations of the second virial coefficient. In Figure 1 are shown the equivalent temperature differences resulting from the use of the Kihara core model rather than the Lennard-Jones (6-12) model. A direct comparison of the calculated vapor pressures is given in Table VIII.

It was observed, and this is shown below, that the vapor pressures calculated using the Lennard-Jones (6-12) model are in good agreement with the experimental vapor pressure data. Because of this agreement, these calculated vapor pressures are believed to be more nearly correct and are recommended as an adequate representation of the true vapor pressure of this substance. These recommended vapor pressure values are tabulated at one degree intervals in Table XIX, Appendix D.

It must be recognized, however, that equally good agreement with the experimentally determined vapor pressures probably could have been obtained using the Kihara core model if the value of the heat of vaporization at the normal boiling point were slightly adjusted. The Lennard-Jones (6-12) model should not necessarily be taken to be a more accurate representation of the second virial coefficient of carbon monoxide in the cryogenic region, but rather, it is simply more consistent with the other selected values of the thermal and physical properties of this material.

2. Comparison with Experimental Vapor Pressures

In Figure 2, the experimental vapor pressures reported by the various investigators described above are compared with those calculated vapor pressures listed in Table XIX, Appendix D, by showing the equivalent temperature differences

($T_{calc} - T_{obs}$), where T_{obs} is the reported temperature (corrected as described below) corresponding to the experimentally determined pressure, and T_{calc} is the temperature which corresponds to this same pressure as determined by interpolation in the table of calculated vapor pressures.

The reported temperatures of Clusius and Teske,[11] Verschoyle,[77] Crommelin et al,[18] and Clayton and Giauque[8] were corrected by Equation (16) of Appendix B. The reported temperatures of Heuse and Otto[36] were corrected by Equation (20) of Appendix B.

The data in the liquid range are in agreement with the calculated values to within about 0.02° K except for the rather scattered data of Clusius and Teske.* Below the triple point, the agreement becomes progressively poorer, but the deviations appear to be rather randomly scattered. This agreement between the calculated and experimental vapor pressures is considered to be good.

An attempt was made to improve the agreement of the data of Clusius and Teske by correcting their reported temperatures on the basis of the equivalent temperature differences between the oxygen and nitrogen vapor pressures used by them for thermometric purposes and those vapor pressures recently calculated for those substances.[61,83] While a shift of about 0.02° K was effected, the scatter of their data was not significantly reduced.

Of some interest is the equation for the vapor pressure of alpha-solid carbon monoxide derived by Clayton and Giauque[8] by methods similar in principle to those used in this work. The equivalent temperature differences of the vapor pressures calculated from that equation are shown in Figure 1 in which T'_{calc} corresponds to T_{obs} of Figure 2.

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*Values of ($T_{obs} - T_{calc}$) for several of the lower temperature points of Clusius and Teske fell well outside the range of Figure 2.

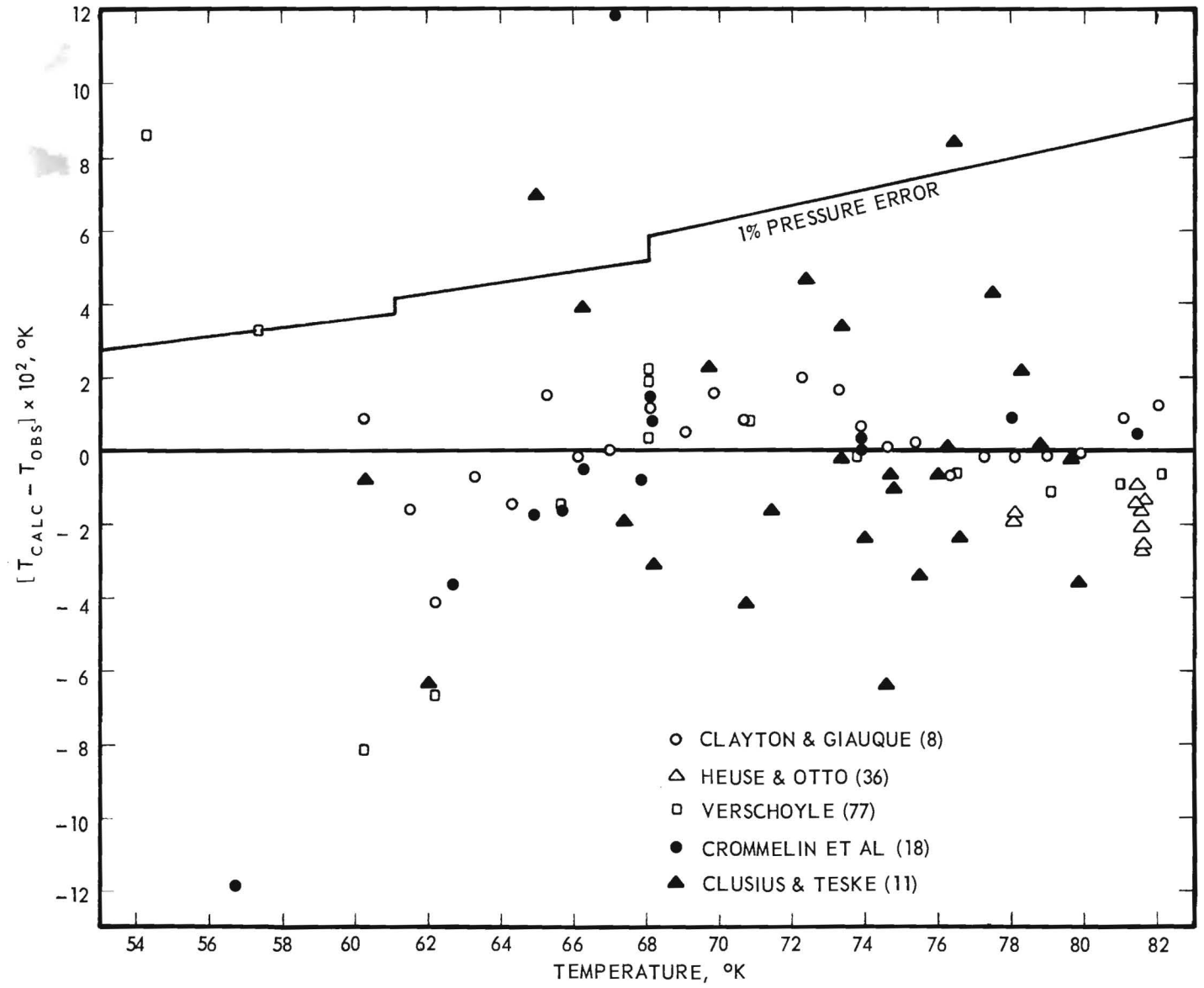

Figure 2. Comparison of Calculated Vapor Pressures with Experimental Values for Carbon Monoxide.

E. Third Law Calculation

A comparison at the normal boiling point of the entropy of carbon monoxide calculated from the calorimetric data used in the vapor pressure calculations with the spectroscopic entropy calculated from Equation (10) using the selected molecular parameters is shown in Table IX. The nonideal gas corrections were made using the Lennard-Jones (6-12) model for the second virial coefficient. The calorimetric entropy contribution from 14° to 44° K was calculated using the heat capacity polynomial fitted to the data of Clayton and Giauque.

Below 14° K, the calorimetric entropy contribution was estimated from the Debye relation with the assumption of 5 degrees of freedom.[6] The Debye parameter, θ_D, was evaluated at 2 degree intervals using the heat capacity values calculated from the least-squares fitted polynomial to which were applied a $c_s' - c_v'$ correction from the Nernst-Lindemann melting point formula. The values of θ_D so obtained for temperatures from 14° to 34° K had a mean value of 106.68° ± 1.41° K. This uncertainty of 1.41° K in θ_D corresponds to an uncertainty in the entropy at 14° K of 0.02 eu.

The use of the heat capacity polynomial fitted to the combined data of Clusius and Eucken below 44° K together with the value of θ_D of 106.24° K (which has an uncertainty of +2.37° and -4.00° K over the temperature range 14° to 34° K) results in a value for the calorimetric entropy at 44° K of 6.175 eu, which may be compared to the value 6.131 eu from Table IX.

The use of the Kihara core model for the second virial coefficient results in a nonideal gas correction of 0.166 eu at the normal boiling point compared with the value 0.132 eu resulting from the use of the Lennard-Jones (6-12) model.

Clayton and Giauque[8] have made a similar third law calculation using their experimental data, the Debye extrapolation assuming 3 degrees of freedom, and

TABLE IX

THIRD LAW CALCULATION FOR CARBON MONOXIDE

	Entropy (eu)	
0° - 14° K (θ_D = 106.68° K, 5 degrees of freedom)	0.559	
14° - 44° K	5.572	
44° - 61.544° K	3.785	
Solid transition at 61.544° K	2.457	
61.544° - 68.127° K	1.238	
Fusion at 68.127° K	2.946	
68.127° - 81.638° K	2.612	
Vaporization to 1 atm gas at 81.638° K	17.683	
Calorimetric entropy of real gas at 1 atm and 81.638° K		36.852
Correction for gas nonideality	0.132	
Calorimetric entropy of ideal gas at 1 atm and 81.638° K		36.984
Spectroscopic entropy from Equation (10)		38.206
Difference		1.222
R ln 2		1.377

the Berthelot equation of state for nonideal gas corrections. They found a difference between the calorimetric and spectroscopic entropy of 1.1 ± 0.1 eu at the normal boiling point, which is considered to be in good agreement with the results shown in Table IX. However, their values of 37.22 eu for the calorimetric entropy and 38.32 eu for the spectroscopic entropy at the normal boiling point are not in such good agreement with those shown in Table IX as

is their difference between these two quantities. The difference between the calorimetric entropies is due largely to the differences in the estimation of the entropy at 14° K and in the gas nonideality correction at the normal boiling point. The difference between the spectroscopic entropies is presumably due to the use of different values for the fundamental constants and molecular parameters. The entropies calculated from Equation (10) are in good agreement with the calculated values given by Goff and Gratch[27] and Hilsenrath et al.[38]

This difference in the calorimetric and spectroscopic entropies is attributed by Clayton and Giauque[8] to the randomness of the orientation of the slightly polar molecules (0.1172 Debye units)[75] in the solid phase which should contribute an additional R ln 2 = 1.377 eu to the calorimetric entropy. It is suggested by them that their observed difference of 1.1 eu might indicate that partial ordering of the dipoles had occurred. This suggestion apparently led Kaischev[42] to search for differences in the heat capacities and heats of transition when the methods and rates of forming the solid phases of carbon monoxide were varied; he was unable to detect any such differences. This result and the uncertainties in some of the calorimetric calculations suggest that there may well be no partial ordering of the dipoles in the solid. Additional calorimetric data would be required to resolve this question.

IV. VAPOR PRESSURE AND HEATS OF SUBLIMATION OF CARBON DIOXIDE

A. Introduction

The vapor pressure and heats of sublimation of carbon dioxide were calculated from its normal sublimation point (194.694° K) to 40° K using appropriate equations from Section II. The calculations were made for the normally occurring isotopic mixture. The thermodynamic properties of the ideal gas at one atmosphere pressure were calculated assuming a rigid-rotator, harmonic-oscillator approximation.

B. Review of Experimental Data for Carbon Dioxide

1. General

The calculation of vapor pressures from Equation (5) and heats of sublimation from Equation (1) for carbon dioxide in the temperature range from the normal sublimation point to 40° K requires the following data: $(\Delta H_v)_{T_1}$; P_1; and c_s' and v_s' as a function of temperature. A representation of the second virial coefficient as a function of temperature is also required. The effect of higher virial coefficients is assumed to be negligible. In addition, the appropriate molecular structure data are required to permit calculation of the thermodynamic properties of the ideal gas.

From a survey of the literature, a selection has been made of the "best" values of these thermal and related properties of carbon dioxide. These selected values are summarized in Table X. The selection of these data is discussed in the following sections. The available experimental data for the vapor pressure of carbon dioxide below one atmosphere have been assembled for comparison with the computed quantities. In addition, the experimental values of the heat of sublimation of Eucken and Donath[21] below one atmosphere are compared with the computed heats of sublimation.

TABLE X

SELECTED PHYSICAL PROPERTIES OF CARBON DIOXIDE

Property	Selected Value	Table No.
Normal sublimation point (nbp) (P = 760 mm Hg)	194.694° K	XI
Heat of sublimation (nbp)	6030 cal/gm mole	XII
Heat capacity of saturated condensed phases	Polynomial for appropriate temperature range	XIII
Mean molal volume of solid		XIII
(194.694° - 101.0° K)	27.40 ml/gm mole	
(101.0° - 38.0° K)	25.90 ml/gm mole	
(38° - 15.0° K)	25.65 ml/gm mole	
Parameters for second virial coefficient function (Kihara core model with quadrupole correction)		
U_o/k	381.97° K	
ρ_o	2.925 Å	
M_o	9.173 Å	
S_o	2.469 $Å^2$	
V_o	0.1781 $Å^3$	
Q^*	0.1793	
Molecular parameters		XIV
Rotational constant, B_o	0.39021 cm^{-1}	
Fundamental wave numbers		
$w_1(1)$[a]	1341.54 cm^{-1}	
$w_2(2)$	667.40 cm^{-1}	
$w_3(1)$	2349.16 cm^{-1}	
Molecular weight	44.011	

[a] Indicates degeneracy of wave numbers.

The temperature of the normal sublimation point and all vapor pressure measurements have been converted where possible to a thermodynamic scale with an ice point of 273.15° K. However, values reported on the International Temperature Scale have been converted to the International Kelvin Scale[70] by the addition of the temperature reported in degrees Celsius to 273.15° K. No attempt was made to correct the International Kelvin Scale to the thermodynamic scale. In the particular range of interest, namely near the normal sublimation point of carbon dioxide, there is an apparent discrepancy between the International Kelvin Scale and the thermodynamic temperature scale. This discrepancy is perhaps as much as 0.05° K. (See e.g. Heuse and Otto[35] and Keesom and Dammers.[44])

2. Normal Sublimation Point of Carbon Dioxide

The values of the normal sublimation point of carbon dioxide of other than historic interest are reported in Table XI. The values reported by Ambrose[1] and Meyers and Van Dusen[56] were reported on the International Temperature Scale and were not considered in deciding on the best value on the thermodynamic scale. The selected value was taken to be an average of the values given by Giauque and Egan[25] and Heuse and Otto.[36]

3. Heats of Sublimation of Carbon Dioxide

The heat of sublimation at one atmosphere pressure has been experimentally measured by Giauque and Egan[26] and Andrews.[2] In addition to these measurements at one atmosphere pressure, Eucken and Donath[21] have measured the heat of condensation of solid carbon dioxide at a number of lower temperatures and report the results at 140° K and 170° K. Maass and Barnes[51] have indirectly determined the heat of sublimation by measuring the enthalpy change from solid

TABLE XI

NORMAL SUBLIMATION POINT OF CARBON DIOXIDE

Reported Temperature	Method of Correction[a]	Corrected Temperature (°K)	Year	Investigator
194.65° K	16	194.693	1913	von Siemens[78]
194.584° K	15	194.620	1914	Henning[31]
- 78.53° C	18	194.614	1921	Keyes et al[45]
- 78.483° C	14	194.670	1931	Heuse and Otto[34]
- 78.471° C	14	194.682	1932	Heuse and Otto[36]
- 78.515° C	21	194.635[b]	1932	Meyers and Van Dusen[56]
- 78.51° C	-	194.64	1935	Aoyama and Kanda[3]
194.67° K	15	194.706	1937	Giauque and Egan[25]
- 78.508° C	21	194.642[b]	1955	Ambrose[1]
	Selected Value	194.694		

[a] See Appendix B for method of correction.

[b] Corrected temperature is on the International Kelvin Scale.

carbon dioxide at -183.1° C to gas at 25° C. The results are summarized below in Table XII. The value of 6030 cal/gm mole obtained by Giauque and Egan was selected as the best value. The results of Eucken and Donath at lower temperatures are compared in Section IV-D with the results calculated from Equation (1).

4. Heat Capacities of Solid Carbon Dioxide

The heat capacity of solid carbon dioxide has been measured by Giauque and Egan[25] (15.52° - 189.78° K), Eucken[20] (19.4° - 88.4° K), and Eucken and Hauck[22] (80° - 210° K). In addition Maass and Barnes[51] measured the enthalpy change for carbon dioxide between the solid or liquid and the gas at 25° C and atmospheric

TABLE XII

HEATS OF SUBLIMATION OF CARBON DIOXIDE

Temperature	Heat of Sublimation (cal/gm mole)	Year	Investigator
(P = 1 atm)	6205 ±35	1925	Andrews[2]
- 78.5° C	6025	1926	Maass and Barnes[51]
140.0° K	6334 ±5	1926	Eucken and Donath[21]
170.0° K	6190 ±5	1926	Eucken and Donath[21]
194.67° K	6030 ±5	1937	Giauque and Egan[25]
Selected Value	6030		

pressure, as a function of temperature. From these data they obtained an equation for the heat capacity of solid carbon dioxide above 78° K. The data of Eucken are almost 4 percent lower than Giauque and Egan between 20° and 30° K while the data of Eucken and Hauck are higher over the range between 80° and 170° K, the maximum deviation being approximately 4 percent. Between 170° K and the normal sublimation temperature, the data of Eucken and Hauck lie slightly below those of Giauque and Egan, while those of Maass and Barnes lies above by as much as 5.8 percent.

The data of Giauque and Egan were fitted to a series of polynomials of the form of Equation (8). From 15° to 38° K, the values of c_s'/T were least squared and thus the value of A_o obtained was identically zero. The values of the coefficients of the polynomials are given in Table XIII. Below 15° K the heat capacity was assumed to be represented by a Debye function with 5 degrees of freedom. The value of θ_D of 167.5 ±0.2° K represented the data of Giauque and Egan between 15° and 20° K.

TABLE XIII

COEFFICIENTS FOR HEAT CAPACITY POLYNOMIALS AND MEAN MOLAL VOLUMES FOR SOLID CARBON DIOXIDE

Range, °K	15-38	38-101	101-195
A_o	0.0	-5.5947076	2.3376821
$A_1 \times 10$	0.85851190	3.7401898	1.1698773
$A_2 \times 10^2$	-1.6808205	-0.33794419	-0.059883313
$A_3 \times 10^3$	1.3620995	0.011507397	0.0014760792
$A_4 \times 10^5$	-3.5205651	0.0	0.0
$A_5 \times 10^7$	3.0349981	0.0	0.0
Mean Molal Volume, ml/gm mole	25.65	25.90	27.40

5. Molal Volumes of Solid Carbon Dioxide

The molal volume of solid carbon dioxide has been determined by Maass and Barnes[51] by measuring the volume change of liquid propane-solid carbon dioxide mixtures as a function of temperature over the range 90.15° to 193.65° K. From the known density of the propane (determined in a separate series of experiments) the density of the solid carbon dioxide was determined. Heuse[37] determined the molal volume at 20° K by measuring the quantity of helium gas displaced by a known quantity of carbon dioxide.

Keesom and Köhler[43] have determined the lattice constants of carbon dioxide from X-ray diffraction studies between 20° and 114° K. These values of the lattice constants were used to compute the molal volume of carbon dioxide. Although the values of the molal volume computed from the lattice constants are approximately 1 percent lower than the values of Heuse at 20° K and Maass and

Barnes at 90° K, these values were used in conjunction with the higher values of Maass and Barnes to obtain the mean molal volumes given in Table XIII. A mean value of the molal volume of the solid phase was assumed to apply over the temperature range of each heat capacity polynomial. The value of the molal volume selected for the uppermost range corresponds to a temperature (164° K) at which the vapor pressure is approximately 0.5 atmosphere. For the lower two polynomials the mean value was simply chosen at the midpoint temperatures, namely 25.90 ml/gm mole at 69.5° K, and 25.65 ml/gm mole at 25° K.

6. Second Virial Coefficient of Carbon Dioxide

The second virial coefficient of carbon dioxide has been represented analytically by Prausnitz and Myers[65] using the Kihara core model[46] with an additional correction for quadrupole interaction. This method of representing the second virial coefficient was selected for the calculations of the vapor pressure and heats of sublimation of carbon dioxide. It was discovered, however, that better agreement of both the calculated virial coefficients at lower temperature with experimental virial data and also of the calculated vapor pressures with the experimental values could be obtained by a slight adjustment of the parameters U_o/k and ρ_o in the potential function. A more complete discussion of this adjustment and the available experimental data is given in Appendix C.

7. Molecular Parameters of Carbon Dioxide

In the temperature range of interest, the molecular parameters needed in the calculation of the thermodynamic properties of the ideal gas at one atmosphere using a rigid-rotator, harmonic-oscillator model are the molecular weight of the normal isotopic mixture, the observed energy changes between the

lowest and next lowest vibration states, and the rotational constant, B_o. Values of the rotational constant, B_o, and the vibrational wave numbers, ω_i, given below in Table XIV were taken from the work of Courtoy.[17] These values are in good agreement with other recent values. These values are for $C^{12}O_2^{16}$. Corrections to the entropy for the naturally occurring isotopic composition were made using the table given by Woolley.[81] The value of the molecular weight of the normally occurring isotopic composition was taken from the compilation of atomic weights by Wichers.[80]

TABLE XIV

MOLECULAR PARAMETERS FOR CARBON DIOXIDE

Quantity		Value		Reference
Vibration Wave Number,	$\omega_1(1)$[a]	1341.54	cm^{-1}	Courtoy[17]
	$\omega_2(2)$	667.40	cm^{-1}	Courtoy[17]
	$\omega_3(1)$	2349.16	cm^{-1}	Courtoy[17]
Rotational Constant,	B_o	0.39021	cm^{-1}	Courtoy[17]
Molecular Weight,	M	44.011		Wichers[80]

[a] Numbers in parentheses indicates degeneracy of the wave number.

8. Experimental Vapor Pressures of Carbon Dioxide

Meyers and Van Dusen[56] reviewed the available experimental vapor pressures prior to 1932; combined the best available data for solid carbon dioxide below the normal sublimation point with their own data, which began at the normal sublimation point and extended to the critical point; and tabulated the results which have been widely accepted as the best vapor pressure tables for carbon dioxide available. The temperatures reported by Meyers and Van Dusen for

their own work are on the International Temperature Scale of 1928.[30] No attempt was made by them to convert the temperatures of the various investigators to a common basis. They remark that with the exception of some data at the triple point, all temperatures differ from the International Temperature Scale by an amount less than the experimental error. Below in Table XV are given the investigators considered by Meyers and Van Dusen, and in addition, those whose

TABLE XV

EXPERIMENTAL VAPOR PRESSURE OF SOLID CARBON DIOXIDE

Investigator	Year	Range	Ice Point (°K)	Method of Temperature Conversion
Onnes and Weber[62]	1913	-183° to -160° C	273.09	16
Weber[79]	1913	-160° to -140° C	273.09	16
von Siemens[78]	1913	145.9° to 195.7° K	273.09	16
Henning and Stock[32]	1921	-109.7° to -80.1° C	273.10	15
Heuse and Otto[34]	1931	- 80.4° to -77.8° C	273.16	14
Heuse and Otto[36]	1932	- 78.5° to -78.1° C	273.16	14
Meyers and Van Dusen[56]	1932	- 78.8° to -56.6° C		21
Giauque and Egan[25]	1937	154.2° to 195.8° K	273.10	15
Tickner and Lossing[71]	1951	-166.7° to -119.5° C	(273.15)[a]	
Ambrose[1]	1956	- 94.7° to -75.4° C		21

[a]No ice point was given. Temperatures were converted to degrees Kelvin by addition of the reported temperatures to 273.15.

work has been done subsequent to 1932. Where possible, the temperature scales of the various investigators were converted to the thermodynamic temperature scale with an ice point of 273.15° K using the methods of conversion listed in column 5 (see Appendix B for temperature conversion) of Table XV.

The data of Meyers and Van Dusen[56] and Ambrose[1] were measured on the International Temperature Scale. These temperatures were converted to the International Practical Kelvin Scale[70] by simply adding the values to 273.15° K.

C. Computational Methods

1. General

The computational methods used to solve Equations (5) and (1) for the vapor pressure and heats of sublimation of carbon dioxide are the same as those described for carbon monoxide in Section III, with the exception of the method used to compute the thermodynamic properties of the ideal gas.

2. Calculation of Ideal Gas Thermodynamic Properties

The ideal gas thermodynamic properties of carbon dioxide were calculated assuming a rigid-rotator, harmonic-oscillator model using the classical equations similar to those of Mayer and Mayer.[55]

$$\frac{H^o - H_o^o}{RT} = \frac{7}{2} + \sum_{i=1}^{4} x_i/(e^{x_i} - 1) \qquad (11)$$

$$\frac{S^o}{R} = \frac{5}{2} \ln T + \frac{3}{2} \ln M - 0.164862 + \sum_{i=1}^{4} \left[x_i/(e^{x_i} - 1) - \ln(1 - e^{-x_i}) \right]$$

$$- \ln 2y + \Delta \qquad (12)$$

In these equations the symbols are the same as in Equations (9) and (10) of Section III with the exception of Δ which is a small entropy correction for the naturally occurring isotopic composition. The value of Δ was taken from Table 3 of Woolley[81] and assumed to be constant and equal to 0.001 eu over the entire temperature range of interest, namely 40° to 194.694° K. The entropy of isotopic mixing is not included in the calculated values for the entropy.

D. Discussion of Results

1. Results of Calculations

From a selection of the best data available for the properties of carbon dioxide as listed in Table X, the values of the vapor pressure and heats of sublimation have been calculated at one degree intervals from the normal sublimation temperature to 40° K. These results are given in Table XX, Appendix E.

In addition two other calculations of the vapor pressures were made which differ only in the methods of representing the second virial coefficient. A comparison of these three calculations is shown in Figure 3. This comparison is based on the temperature deviation, $T_{CALC}-T'_{CALC}$, where T_{CALC} is the temperature corresponding to a vapor pressure in Table XX (calculated from the parameters in Table X), and T'_{CALC} is the temperature at that same vapor pressure calculated using one of the two other virial coefficient representations. Curve A was obtained using the Lennard-Jones (6-12) intermolecular potential function with the parameters of MacCormack and Schneider.[50] Curve B was obtained using the Kihara core model with quadrupole corrections and the parameters of Prausnitz and Myers.[65]

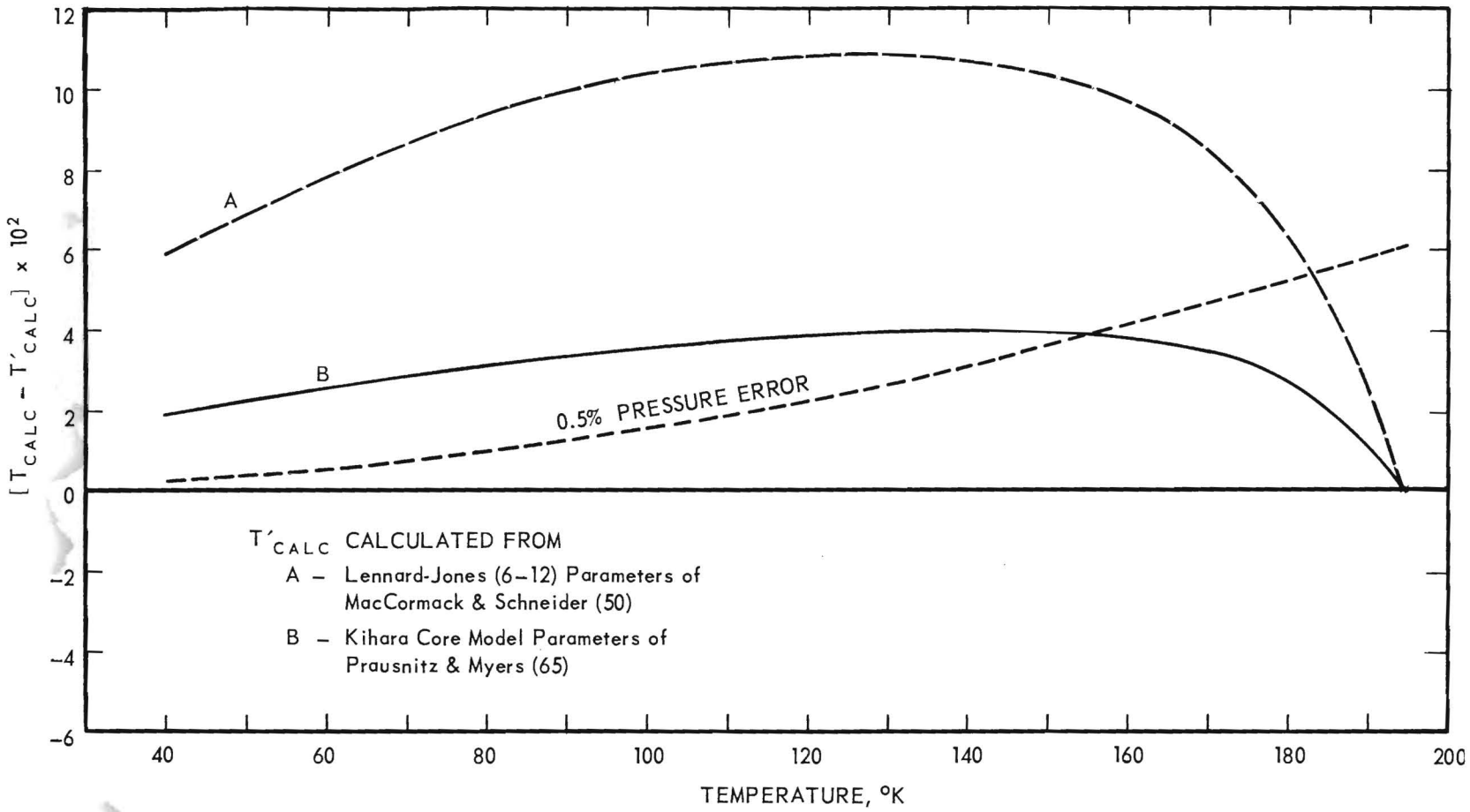

Figure 3. Comparison of Calculated Vapor Pressures of Carbon Dioxide for Different Second Virial Coefficient Representations.

2. Comparison of Calculated with Experimental Vapor Pressures

In Figure 4 is shown a comparison of the calculated vapor pressures given in Table XX with the experimental data of Giauque and Egan,[25] Ambrose,[1] and sublimation points of Heuse and Otto,[34, 36] and Aoyama and Kanda.[3] Also shown in Figure 4 is the difference between the thermodynamic scale and the International Temperature Scale as determined by Keesom and Dammers,[44] who compared a helium gas thermometer with five different platinum resistance thermometers. It is interesting to note that had the data of Ambrose been corrected according to this curve, the agreement with the calculated vapor pressures would have been comparable to that of Giauque and Egan, which is considered to be very good.

In Figure 5 is shown the remainder of the vapor pressures considered in this work, including the vapor pressures represented by Equation (9) of Meyers and Van Dusen. This equation was based on all the available data prior to 1932 including their own data which extended down to the normal sublimation point. These data do not show such good agreement as do those shown in Figure 4; however, in the low pressure region (below 140° K) the deviations appear to be random.

3. Comparison of Calculated Heats of Sublimation with Experimental Values of Eucken and Donath

Eucken and Donath[21] have reported values of the heat of sublimation of carbon dioxide at 140° and 170° K. These values are compared in Table XVI with the heats of sublimation calculated from Equation (1) using the physical properties of carbon dioxide listed in Table X. In addition the results obtained using the two other second virial coefficient representations shown in Figure 7 and discussed in Section 1 above and Appendix C are compared with the experimental values. The heats of sublimation calculated from the physical properties

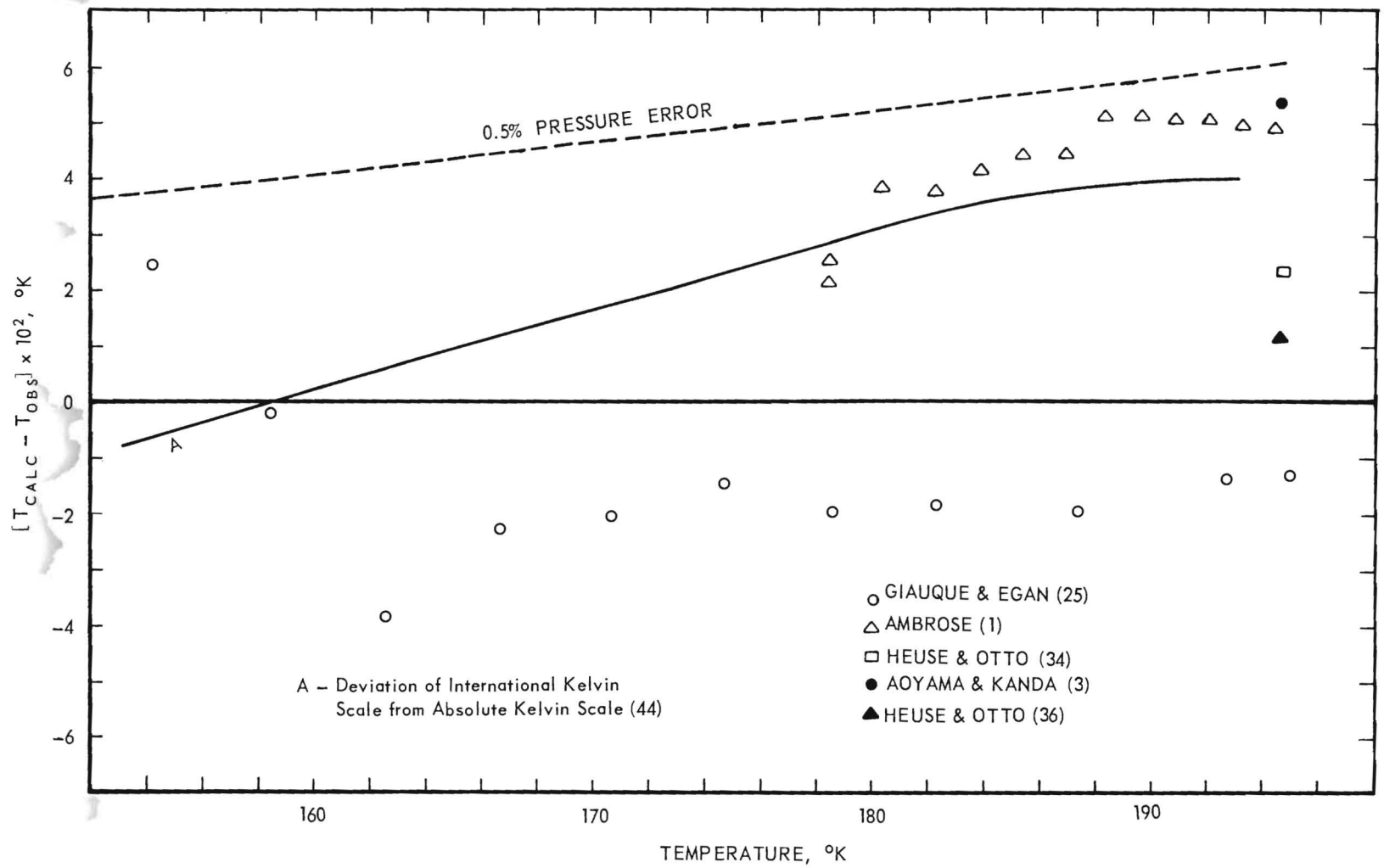

Figure 4. Comparison of Calculated Vapor Pressures with Selected Experimental Values for Carbon Dioxide.

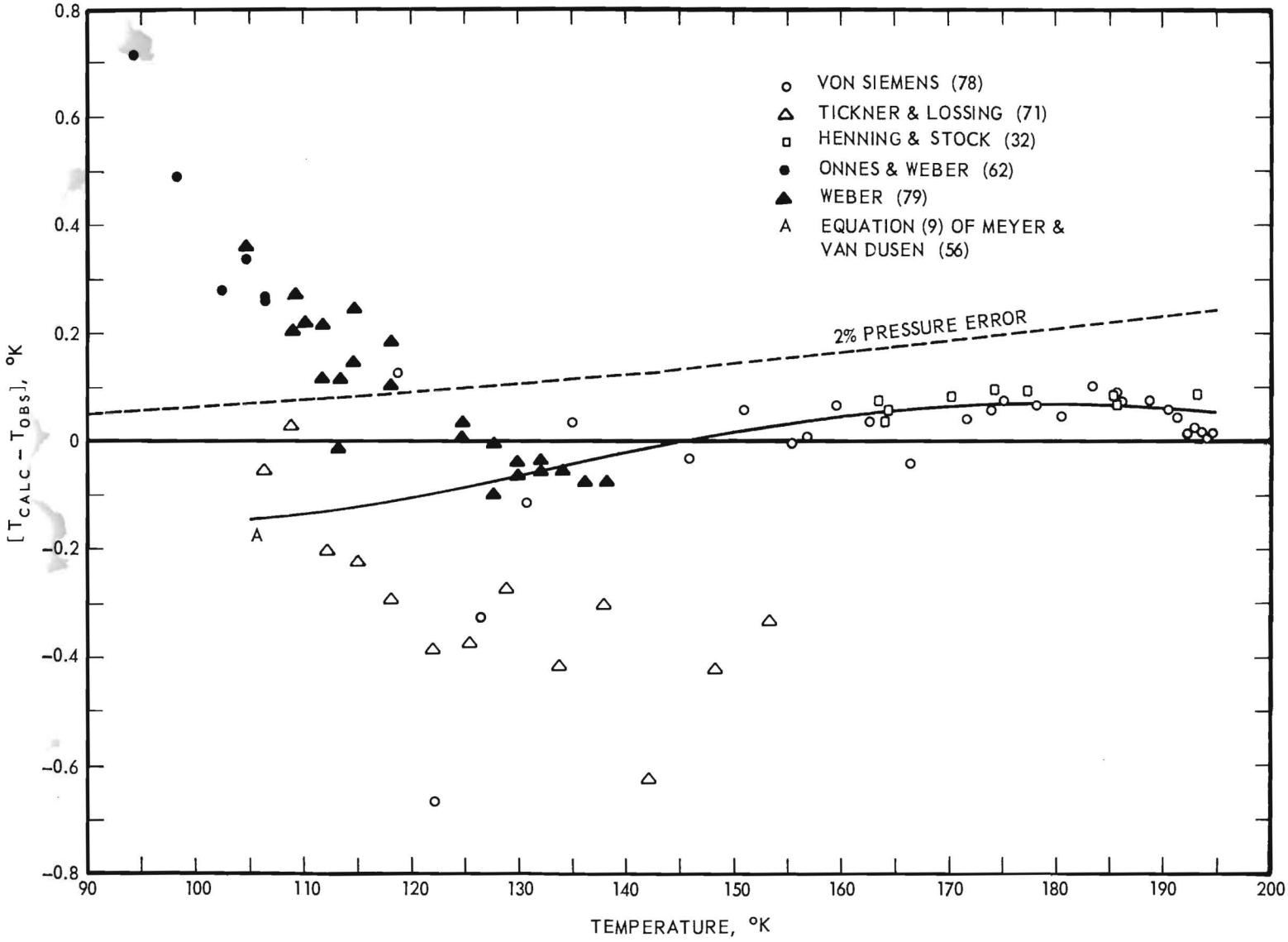

Figure 5. Comparison of Calculated Vapor Pressures with Experimental Values for Carbon Dioxide.

listed in Table X agree with the experimental values slightly better than the other two methods of calculation. This better agreement lends support to the use of the selected physical properties for the calculation of vapor pressures.

TABLE XVI

COMPARISON OF CALCULATED AND EXPERIMENTAL HEATS OF SUBLIMATION OF CARBON DIOXIDE

Temperature (°K)	Heat of Sublimation (cal/gm mole)			
	(a)	(b)	(c)	(d)
140	6334±5	6317.3	6313.8	6306.2
170	6190±5	6183.9	6180.8	6174.5

[a] Experimental values of Eucken and Donath[21]

[b] Calculated from Equation (1) using the parameters given in Table X.

[c] Same as (b) except that virial coefficients were represented using the Kihara core model with quadrupole corrections and the parameters of Prausnitz and Meyers.[65]

[d] Same as (b) except that virial coefficients were represented using the Lennard-Jones (6-12) function and the constants of MacCormack and Schneider.[50]

E. Third Law Calculation

A comparison at the normal sublimation point (194.694° K) of the entropy of carbon dioxide calculated from the calorimetric data used in the vapor pressure calculations, with the spectroscopic entropy calculated from Equation (12), is given in Table XVII. The nonideal gas correction was made assuming gas to be represented by Equation (3) with the second virial coefficient represented by the Kihara core model using the adjusted values of the parameters given in Table X.

Below 15° K, the calorimetric entropy was estimated from the Debye relation with the assumption of 5 degrees of freedom.[6] The value of 167.5° K for the Debye parameter, θ_D, was found to represent the experimental heat capacity data from 15° to 20° K, and was used to evaluate the entropy below 15° K.

Giauque and Egan[25] have made a third law calculation using the same thermal data. However, their value of θ_D was based on 3 degrees of freedom and for the gas nonideality correction the Berthelot equation of state was used. They report values of 47.59 and 47.55 eu respectively for the calorimetric and spectroscopic entropies at 194.67° K. The values reported in Table XVII are in agreement with those reported by Giauque and Egan.

TABLE XVII

THIRD LAW CALCULATION FOR CARBON DIOXIDE

	Entropy (eu)	
0° - 15° K (θ_D = 167.5° K, 5 degrees of freedom)	0.185	
15° - 38° K	1.968	
38° - 101° K	7.039	
101° - 194.694° K	7.324	
194.694° K (sublimation to 1 atm. gas)	30.972	
Calorimetric entropy of real gas at 1 atm. and 194.694° K		47.488
Correction for gas nonideality	0.106	
Calorimetric entropy of ideal gas at 1 atm. and 194.694° K		47.594
Spectroscopic entropy from Equation (12)		47.562
Difference		.032

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Respectfully submitted:

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Approved:

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VII. APPENDIXES

A. Nomenclature and Physical Constants*

B	=	second virial coefficient of gas.
B_o	=	$h/8\pi^2 cI = 2.79832 \times 10^{-39}/I$ (gm-cm^2)
b_o, e/k	=	parameters used in the Lennard-Jones (6-12) intermolecular potential function.
c	=	velocity of light = 2.99702×10^{10} cm/sec.
c_s'	=	molal heat capacity of saturated condensed phase.
F_1, F_2, F_3	=	functions in the Kihara core model for the second virial coefficient, defined by Equation (24).
H_{10}	=	function for quadrupole interaction, defined by Equation (28).
h	=	Planck constant = 6.62377×10^{-27} erg-sec/molecule.
$(\Delta H_v)_T$	=	heat of vaporization (or sublimation) at T.
(ΔH_{tr})	=	heat of transition of condensed phase at transition temperature, T_{tr}.
$\sum_{T}^{T_1} (\Delta H_{tr})$	=	sum of all condensed phase transitions from T to T_1.
$(H^o - H_o^o)_T''$	=	enthalpy function for ideal gas at T.
I	=	moment of inertia.
k	=	Boltzmann constant = 1.38038×10^{-16} erg/°K-molecule.
M	=	molecular weight
M_o, S_o, V_o	=	parameters of Kihara core model.
N_o	=	Avogadro's Number = 6.02380×10^{23} molecules/gm mole.
P	=	pressure.
P_1, T_1	=	pressure and temperature of a fixed point on the vapor pressure curve.

*The physical constants used were those of Rossini et al, J. Am. Chem. Soc. 74, 2699 (1952) adjusted to an ice point of 273.150° K.

Q = molecular quadrupole moment.

Q^* = reduced quadrupole moment (dimensionless).

R = gas constant = 1.98726 cal/gm mole °K = 0.0820574 liter atm/gm mole °K. (1 calorie = 4.1840 ab. joules = 4.1833 int. joules).

$S^o(P,T)''$ = entropy of the ideal gas at P and T.

$(S^o)''_T$ = entropy of ideal gas at P = 1 atm and T.

T = temperature on the thermodynamic scale with an assigned ice point of 273.15° K.

T^* = temperature on the Kelvin Scale used by individual investigator.

t^* = temperature on the Celsius Scale used by individual investigator.

t = degree Celsius. Also used as dummy variable in Equation (24).

U = potential energy between molecules.

U_o = minimum potential energy between molecules.

V = molal volume of gas.

v'_s = molal volume of saturated condensed phase.

y = hcB_o/kT

Z = U_o/kT

Δ = difference between the entropy of the normally occurring isotopic mixture of CO_2 and that of $C^{12}O^{16}_2$.

δ = defined by Equation (2) and Equation (4).

ε = defined by Equation (6) and Equation (7).

ρ = shortest distance between molecular cores.

ρ_o = shortest distance between molecular cores at minimum potential energy.

σ = separation of molecular centers at zero potential energy.

Superscripts

$'$ = condensed phase

$''$ = gas phase

* = refers to temperature scale of individual investigator.

Subscripts

O_2 = normal boiling point of oxygen.

s = saturated vapor or condensed state.

v = vaporization. Also refers to sublimation for temperatures at and below the triple point.

B. Conversion of Temperature Scales

The conversion of temperatures reported by a given investigator to a consistent thermodynamic scale based on an ice point, T_o, of 273.150° K has been made where possible. The "best" value for the normal boiling point of oxygen on this scale has been taken to be 90.168° K, the value selected by van Dijk.[74] The various methods used for making these corrections are given below. The final corrected thermodynamic temperature (in °K) used in this paper is represented by T; the temperature reported by the investigator is represented by T^*. In cases where the original temperatures were reported in °C, these were converted to T^* by addition to the reported ice point T_o^*. When no ice point was given, the reported temperature in °C was added to 273.150° to obtain T in °K.

The relations used for making temperature scale conversions were:

1. Methods Involving Only Ice Point Ratios

$$T = T^*(T_o/T_o^*) \qquad (13)$$

$$T = T^*(273.15/273.16) \qquad (14)$$

$$T = T^*(273.15/273.10) \qquad (15)$$

$$T = T^*(273.15/273.09) \qquad (16)$$

$$T = T^*(273.15/273.20) \qquad (17)$$

$$T = T^*(273.15/273.13) \qquad (18)$$

This method of conversion of a thermodynamic temperature scale from one ice point to another is strictly correct only if the ice point temperature is a defined point. When T_o is obtained from a gas thermometer scale defined at the ice point and normal boiling point of water, a more complicated relation is required for exact conversion. (See, for instance, van Dijk).[74] Data for making the exact conversions are not always given by the investigator. However, the exact relations reduce to the simple relation used here in the first approximation. Henning and Otto[33] have used a somewhat different approximate method for correction. Their relation gave the same results as Equation (13) to about 0.002°.

2. Methods Involving Only the Oxygen Point

In the event the oxygen point of a particular scale was well known, and it was desired to correct temperatures based on this known point, they were corrected by

$$T = T^* (T_{O_2}/T_{O_2}{}^*) \tag{19}$$

$$T = T^* (90.168/90.195) \tag{20}$$

3. Method of Correcting International Temperature Scale

Temperatures reported by various investigators on the International Temperature Scale were converted to the International Kelvin Scale by the relation

$$T(\text{Int. } 1948) = t^* + 273.15 \tag{21}$$

No attempt was made to correct the International Kelvin Scale to the thermodynamic scale.

C. Second Virial Coefficients

1. Methods of Calculation

Two analytical representations were used for the second virial coefficients. One of these, based on the Lennard-Jones (6-12) intermolecular potential model, is well known.[39,83] The other representation is the Kihara core model[46] with a (6-12) intermolecular potential function as described by Prausnitz and Myers.[65]

Kihara[46] has derived general expressions for the second virial coefficient of gases assuming an impenetrable core for the gas molecule rather than the point center model used in the Lennard-Jones model. This core may be any convex shaped model and is normally determined from the geometry of the molecule. The potential energy is written as a function of the shortest distance between molecular cores, which for the (6-12) intermolecular potential function is

$$U = U_o\left[\left(\frac{\rho_o}{\rho}\right)\right]^{12} - 2\left(\frac{\rho_o}{\rho}\right)^{6}\Bigg] \tag{22}$$

The second virial coefficient is then written as

$$\frac{B}{N_o} = \frac{2\pi}{3}\rho_o{}^3F_3 + M_o\rho_o{}^2F_2 + \left(S_o + \frac{M_o^2}{4\pi}\right)\rho_oF_1 + \left(V_o + \frac{M_oS_o}{4\pi}\right) \tag{23}$$

The functions F_1, F_2, and F_3 are functions of Z ($Z = Uo/kT$) and may be obtained from tabulated results† or calculated from Equation (24)

$$F_s = -\frac{s}{12}\sum_{t=0}^{\infty}\left[\frac{2^t}{t!}\Gamma\left(\frac{6t-s}{12}\right)\right]Z^{(6t+s)/12} \tag{24}$$

---

†The functions have been tabulated by Connolly and Kandalic[13] with Z as the argument from 0.01 to 7.0 in steps of 0.01.

The parameters M_o, S_o, and V_o can be calculated directly from the size and shape of the core.

Prausnitz and Myers[65] have determined the parameters for the Kihara core model for a number of molecules, including carbon monoxide and carbon dioxide. In addition they have taken into account the contribution of the quadrupole moment in carbon dioxide by assuming that the second virial coefficient is given by

$$B = B_{Kihara} + B_{quadrupole} \tag{25}$$

The value of the quadrupole contribution was calculated from the relation of Pople,[64]

$$B_{quadrupole} = -\frac{2}{3}\pi N_o \sigma^3 \left(\frac{7}{320}\right) Q^{*2} H_{10}(Z) \tag{26}$$

where the dimensionless quantity Q^* is related to the quadrupole moment Q by the relation

$$Q^* = \frac{Q^2}{U_o \sigma^5} \tag{27}$$

and σ is related approximately to ρ_o by the relation

$$\sigma = 2^{-1/6}\rho_o + \frac{M_o}{2\pi} \tag{28}$$

This relation is exact for spherical cores.

The function H_{10} was calculated from Equation (29) which was taken from Pople[64]

$$H_{10}(Z) = 2^{17/6} Z^{17/12} \sum_{p=0}^{\infty} \frac{2^p Z^{p/2}}{p!} \Gamma\left(\frac{6p+7}{12}\right) \tag{29}$$

2. Second Virial Coefficients of Carbon Monoxide

a. Experimental Data. Deming and Shupe[19] have reviewed and, in some cases, corrected the earlier P-V-T data for carbon monoxide and have found that the second virial coefficients derived therefrom may be represented between -70° and 400° by Equation (30).

$$B(\text{cc/gm mole}) = 58.05 - 19.84/T \tag{30}$$

More recently, Michels et al[57] have measured P-V isotherms for carbon monoxide over the range 0° to 140° C and from these measurements have derived values for the second virial coefficient.

It appears that the only value for the second virial coefficient of carbon monoxide which has been determined at cryogenic temperatures is the one value at 90.76° K which was reported by Mathot et al.[54]

The data of Michels et al and of Mathot et al are shown in Figure 6 as is the correlation of Deming and Shupe.

b. Analytical Representations. Michels et al[57] reported values for the parameters of the Lennard-Jones (6-12) model of $e = 140.3 \times 10^{-16}$ erg and $\sigma = 3.793 \times 10^{-8}$ cm ($e/k = 101.64°$ K and $b_o = 68.85$ cc/gm mole) which they obtained by fitting their experimental data. Jansen, Michels, and Lupton[40] more recently have quoted, without additional comment, the values $e = 138.2 \times 10^{-16}$ erg and $\sigma = 3.77 \times 10^{-18}$ cm ($e/k = 100.12°$ K

and b_o = 67.60 cc/gm mole) based on the same experimental data. Since the values of the second virial coefficient calculated using the later set of parameters are in better agreement with the experiment data of Michels et al, they were selected for use with the Lennard-Jones (6-12) model.

By fitting the experimental data of Michels et al, Prausnitz and Myers[65] determined values for the parameters of the Kihara core model assuming a sphero-cylindrical core with no quadrupole,† dipole, or quantum corrections. Their parameters are U_o/k = 145.35° K, ρ_o = 3.225 Å, M_o = 4.800 Å, S_o = 0.8344 Å^2, and V_o = 0.03963 Å^3.

Curves calculated using the Lennard-Jones (6-12) and the Kihara core models are shown in Figure 6.

3. Second Virial Coefficients of Carbon Dioxide

a. Experimental Data. The experimental second virial coefficient data for carbon dioxide considered in this work are summarized below in Table XVIII. The data below 400° K are shown in Figure 7 along with analytical representations of the data, which are discussed below. The only data near the normal sublimation point of carbon dioxide are those of Schäfer[68] and Cook.[14] The reliability of both of these investigators is subject to question because of the scatter and poor agreement of their data with that of other investigators at higher temperatures.

b. Analytical Representations. MacCormack and Schneider[50] attempted to determine the best set of parameters for the Lennard-Jones (6-12) intermolecular potential function, but decided that only by using two sets of constants

† It is interesting to note that values for the quadrupole moment of carbon monoxide have been reported and are slightly larger than the reported values for nitrogen.[41]

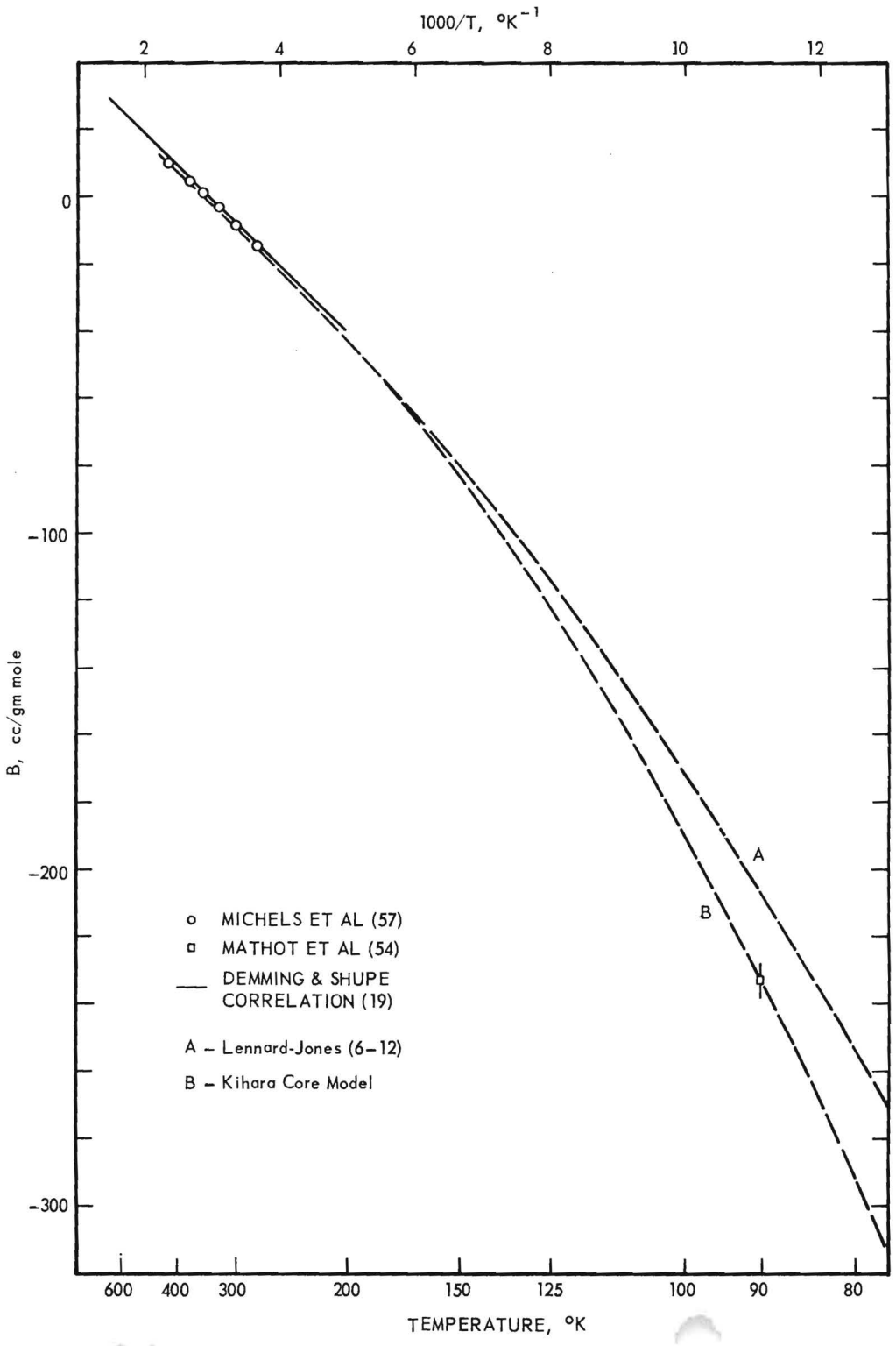

Figure 6. Second Virial Coefficient of Carbon Monoxide.

could the second virial coefficient be represented adequately over the temperature range 0° to 600° C. The representation obtained using the parameters determined by them for the 0° to 200° C region (e/k = 187.5° K, b_o = 113.0 cc/gm mole) is shown in Figure 7. The parameters were fitted to their own data and the data of Michels and Michels.[58]

Prausnitz and Myers[65] have obtained the parameters for the Kihara core model with a (6-12) intermolecular potential function (plus an additional correction for quadrupole interaction) using the second virial coefficient data of Cook,[14] MacCormack and Scheider,[49] Michels and Michels[58] and Schäfer.[68] The molecular core of carbon dioxide was assumed to be a spherocylinder. Values of the parameters determined by Prausnitz and Myers are U_o/k = 380.2° K,

TABLE XVIII

EXPERIMENTAL SECOND VIRIAL COEFFICIENTS OF CARBON DIOXIDE

Range	Year	Investigator
0° to 600° C	1950	MacCormack and Schneider[49]
- 30° to 25° C	1931	Cooper and Maass[15]
0° to 150° C	1935	Michels and Michels[58]
30° to 60° C	1956	Cottrell and Hamilton[16]
- 60° to 30° C	1957	Cook[14]
- 30° to 75° C	1961	Turlington and McKetta[72]
203° to 273.15° K	1937	Schäfer[68]

ρ_o = 2.79 Å, M_o = 9.173 Å, S_o = 2.469 Å^2, V_o = 0.1781 Å^3, and Q^* = 0.1793. It may be noted in Figure 7 that the second virial coefficients calculated from these parameters, although considerably lower than the second virial

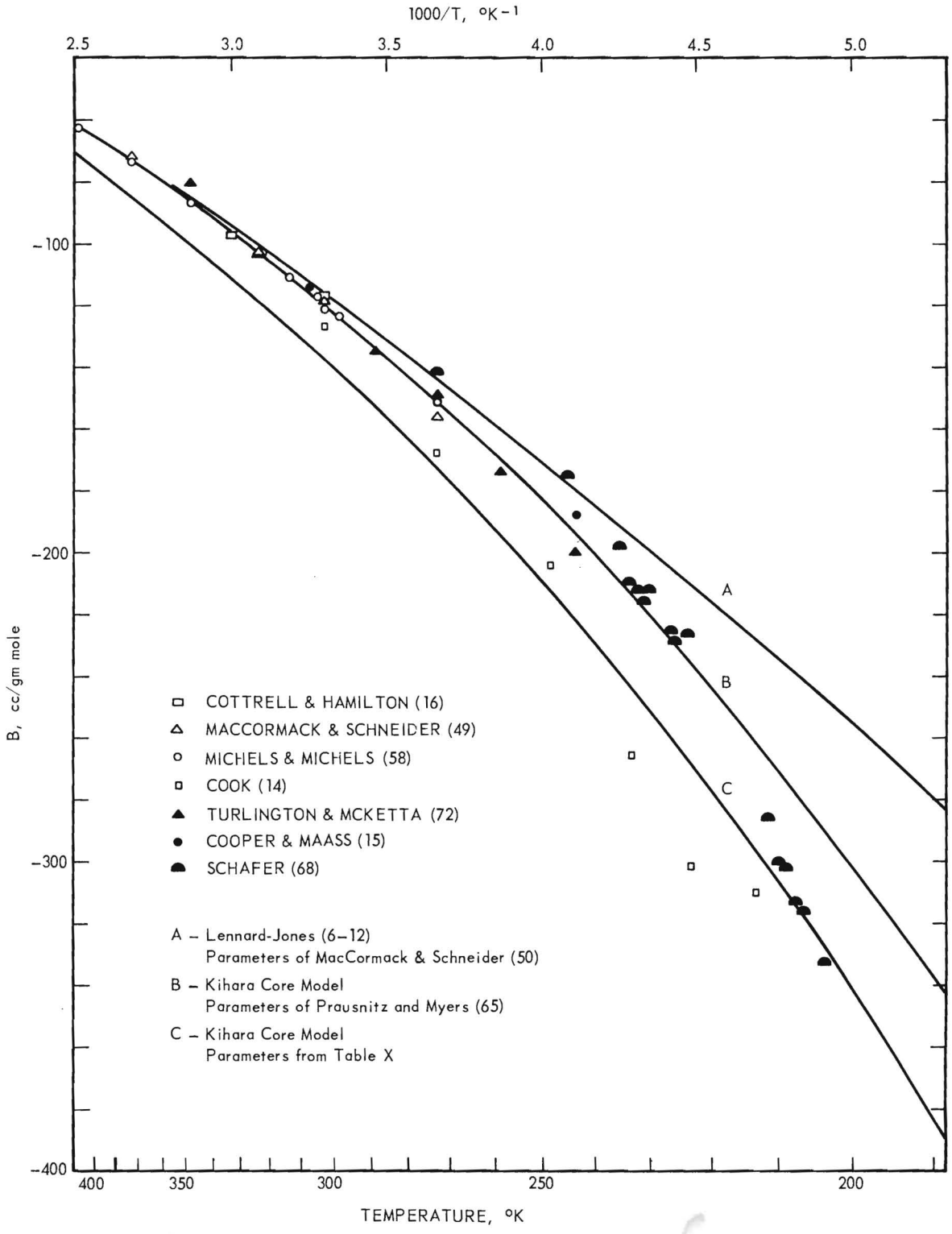

Figure 7. Second Virial Coefficient of Carbon Dioxide.

coefficients calculated from the Lennard-Jones (6-12) intermolecular parameters of MacCormack and Schneider, are still somewhat higher than the experimental data of Schäfer and Cook at the lowest temperatures.

The second virial coefficient representation of Prausnitz and Myers (Curve B, Figure 7 was used to calculate vapor pressures and heats of sublimation from Equation (5) and (1) and the other data as given in Table X. These calculations indicated that better agreement between calculated and experimental vapor pressures could be attained if the second virial coefficient curve were in better agreement with the experimental data at the lower temperatures. Therefore the values of U_o/k and ρ_o were adjusted to 381.97° K and 2.925 Å respectively. The second virial coefficient representation calculated from this adjusted set of parameters is shown in Figure 7. These adjusted parameters do not produce a good fit to all of the available second virial coefficient data; however, they do produce a good fit to the low temperature data of Cook[14] and Schäfer[68] and, moreover, when they are used together with the other data in Table X, a better agreement is obtained between the calculated and observed vapor pressures of carbon dioxide.

This adjusted set of parameters (shown in Table X) was used to compute the vapor pressure and heats of sublimation of carbon dioxide shown in Table XX, Appendix E.

D. Vapor Pressure and Heats of Vaporization and Sublimation of Carbon Monoxide at One Degree Intervals

The results of the calculations for the vapor pressure and heats of vaporization and sublimation for carbon monoxide are given in Table XIX at one degree intervals from the normal boiling point to 14° K. Also included for aid in interpolation are the values $(1/T) \times 10^2$ and $\text{Log}_{10}P$ (P in mm Hg).

These values were computed using the selected data shown in Table I together with the Lennard-Jones (6-12) model for the second virial coefficient and the low temperature (14° to 44° K) heat capacity polynomial fitted to the data of Clayton and Giauque.[8]

TABLE XIX

VAPOR PRESSURE AND HEATS OF VAPORIZATION
AND SUBLIMATION OF CARBON MONOXIDE

Temperature, T (°K)	Pressure, P (mm Hg)	Heat of Vaporization (cal/gm mole)	100/T ($°K^{-1}$)	Log P
- - - - - - - - - - - - - - - - - -	Liquid	- - - - - - - - - - - - - - - - - -		
81.638 (nbp)	760.000	1443.6	1.22492	2.880814
81.000	706.284	1449.4	1.23456	2.848979
80.000	627.996	1458.5	1.25000	2.797956
79.000	556.546	1467.4	1.26582	2.745501
78.000	491.531	1476.3	1.28205	2.691551
77.000	432.552	1485.0	1.29870	2.636039
76.000	379.223	1493.6	1.31578	2.578895
75.000	331.166	1502.2	1.33333	2.520045
74.000	288.010	1510.6	1.35135	2.459408
73.000	249.408	1519.0	1.36986	2.396911
72.000	215.010	1527.3	1.38888	2.332459
71.000	184.485	1535.5	1.40845	2.265962
70.000	157.515	1543.7	1.42857	2.197322
69.000	133.793	1551.8	1.44927	2.126435
68.127 (tp)	115.512	1558.8	1.46784	2.062629
- - - - - - - - - - - - - - - - - -	β-solid	- - - - - - - - - - - - - - - - - -		
68.127 (tp)	115.512	1759.5	1.46784	2.062629
68.000	112.714	1760.2	1.47058	2.051980
67.000	92.604	1766.2	1.49253	1.966628

(Continued)

TABLE XIX (Continued)

VAPOR PRESSURE AND HEATS OF VAPORIZATION
AND SUBLIMATION OF CARBON MONOXIDE

Temperature, T (°K)	Pressure, P (mm Hg)	Heat of Vaporization (cal/gm mole)	100/T ($°K^{-1}$)	Log P
66.000	75.599	1772.0	1.51515	1.878514
65.000	61.306	1777.8	1.53846	1.787503
64.000	49.368	1783.3	1.56250	1.693447
63.000	39.463	1788.7	1.58730	1.596195
62.000	31.303	1794.0	1.61290	1.495582
61.544 (tr.)	28.089	1796.4	1.62485	1.448537
- - - - - - - - - - - - - - - - - - - -		α-solid		- - - - - - - - - - - - - - - - - - - -
61.544 (tr.)	28.089	1947.6	1.62485	1.448537
61.000	24.356	1952.2	1.63934	1.386605
60.000	18.600	1960.0	1.66667	1.269511
59.000	14.062	1967.1	1.69491	1.148047
58.000	10.520	1973.7	1.72413	1.022011
57.000	7.784	1979.7	1.75438	0.891182
56.000	5.693	1985.2	1.78571	0.755324
55.000	4.113	1990.4	1.81818	0.614177
54.000	2.934	1995.1	1.85185	0.467462
53.000	2.065	1999.5	1.88679	0.314885
52.000	1.433	2003.6	1.92307	0.156115
51.000	9.791 (-1)[a]	2007.4	1.96078	-0.009191
50.000	6.586 (-1)	2011.0	2.00000	-0.181410
49.000	4.356 (-1)	2014.3	2.04081	-0.360961

(Continued)

TABLE XIX (Continued)

VAPOR PRESSURE AND HEATS OF VAPORIZATION
AND SUBLIMATION OF CARBON MONOXIDE

Temperature, T (°K)	Pressure, P (mm Hg)	Heat of Vaporization (cal/gm mole)	100/T ($°K^{-1}$)	Log P
48.000	2.830 (-1)	2017.4	2.08333	-0.548282
47.000	1.804 (-1)	2020.2	2.12765	-0.743854
46.000	1.127 (-1)	2022.8	2.17391	-0.948200
45.000	6.888 (-2)	2025.2	2.22222	-1.161888
44.000	4.116 (-2)	2027.3	2.27272	-1.385538
43.000	2.400 (-2)	2029.2	2.32558	-1.619824
42.000	1.363 (-2)	2031.0	2.38095	-1.865489
41.000	7.528 (-3)	2032.6	2.43902	-2.123346
40.000	4.034 (-3)	2033.9	2.50000	-2.394287
39.000	2.093 (-3)	2035.0	2.56410	-2.679293
38.000	1.048 (-3)	2035.8	2.63157	-2.979445
37.000	5.059 (-4)	2036.5	2.70270	-3.295938
36.000	2.344 (-4)	2036.9	2.77778	-3.630100
35.000	1.039 (-4)	2037.1	2.85714	-3.983407
34.000	4.390 (-5)	2037.0	2.94117	-4.357508
33.000	1.761 (-5)	2036.7	3.03030	-4.754249
32.000	6.673 (-6)	2036.2	3.12500	-5.175705
31.000	2.376 (-6)	2035.5	3.22580	-5.624216
30.000	7.899 (-7)	2034.6	3.33333	-6.102430
29.000	2.436 (-7)	2033.4	3.44827	-6.613359
28.000	6.911 (-8)	2032.0	3.57142	-7.160439

(Continued)

TABLE XIX (Continued)

VAPOR PRESSURE AND HEATS OF VAPORIZATION
AND SUBLIMATION OF CARBON MONOXIDE

Temperature, T (°K)	Pressure, P (mm Hg)	Heat of Vaporization (cal/gm mole)	100/T ($°K^{-1}$)	Log P
27.000	1.788 (-8)	2030.4	3.70370	-7.747608
26.000	4.174 (-9)	2028.5	3.84615	-8.379403
25.000	8.688 (-10)	2026.5	4.00000	-9.061081
24.000	1.589 (-10)	2024.1	4.16666	-9.798761
23.000	2.514 (-11)	2021.6	4.34782	-10.599619
22.000	3.372 (-12)	2018.7	4.54545	-11.472111
21.000	3.747 (-13)	2015.6	4.76190	-12.426289
20.000	3.356 (-14)	2012.2	5.00000	-13.474195
19.000	2.342 (-15)	2008.5	5.26315	-14.630374
18.000	1.223 (-16)	2004.6	5.55555	-15.912567
17.000	4.543 (-18)	2000.3	5.88235	-17.342647
16.000	1.127 (-19)	1995.6	6.25000	-18.947904
15.000	1.726 (-21)	1990.7	6.66666	-20.762836
14.000	1.473 (-23)	1985.4	7.14285	-22.831718

[a]Numbers in parentheses indicate powers of 10 by which pressure entry is to be multiplied; thus 9.791 (-1) = 0.9791.

E. Vapor Pressure and Heats of Sublimation of Carbon Dioxide at One Degree Intervals

The results of the calculations for the vapor pressure and heats of sublimation for carbon dioxide are given in Table XX at one degree intervals from the

normal sublimation point to 40° K. These values were computed using the data listed in Table X. Also included for aid in interpolation are the values $(1/T) \times 10^2$ and Log_{10} P(P in mm Hg).

TABLE XX

VAPOR PRESSURE AND HEATS OF SUBLIMATION OF CARBON DIOXIDE

Temperature, T (°K)	Pressure, P (mm Hg)	Heat of Sublimation (cal/gm mole)	$(1/T) \times 10^2$ ($°K^{-1}$)	Log P (P in mm Hg)
194.694	760.000	6030.0	0.513627	2.880814
194	717.767	6035.4	0.515463	2.855983
193	660.540	6042.9	0.518134	2.819899
192	607.372	6050.3	0.520833	2.783455
191	558.006	6057.6	0.523560	2.746639
190	512.203	6064.7	0.526315	2.709442
189	469.740	6071.7	0.529100	2.671858
188	430.404	6078.5	0.531914	2.633876
187	393.994	6085.2	0.534759	2.595490
186	360.321	6091.8	0.537634	2.556690
185	329.207	6098.3	0.540540	2.517469
184	300.481	6104.6	0.543478	2.477817
183	273.985	6110.9	0.546448	2.437726
182	249.567	6117.0	0.549450	2.397188
181	227.086	6123.0	0.552486	2.356191
180	206.410	6129.0	0.555555	2.314730
179	187.410	6134.8	0.558659	2.272793
178	169.970	6140.6	0.561797	2.230372

(Continued)

TABLE XX (Continued)

VAPOR PRESSURE AND HEATS OF SUBLIMATION OF CARBON DIOXIDE

Temperature, T (°K)	Pressure, P (mm Hg)	Heat of Sublimation (cal/gm mole)	$(1/T) \times 10^2$ ($°K^{-1}$)	Log P (P in mm Hg)
177	153.977	6146.3	0.564971	2.187457
176	139.328	6151.9	0.568181	2.144040
175	125.924	6157.4	0.571428	2.100108
174	113.671	6162.8	0.574712	2.055653
173	102.486	6168.2	0.578034	2.010665
172	92.286	6173.5	0.581395	1.965134
171	82.994	6178.8	0.584795	1.919048
170	74.542	6183.9	0.588235	1.872398
169	66.861	6189.0	0.591715	1.825171
168	59.890	6194.1	0.595238	1.777354
167	53.573	6199.1	0.598802	1.728944
166	47.855	6204.0	0.602409	1.679924
165	42.686	6208.9	0.606060	1.630282
164	38.020	6213.8	0.609756	1.580007
163	33.813	6218.5	0.613496	1.529086
162	30.027	6223.3	0.617283	1.477506
161	26.623	6228.0	0.621118	1.425255
160	23.568	6232.6	0.625000	1.372320
159	20.830	6237.2	0.628930	1.318687
158	18.380	6241.8	0.632911	1.264342
157	16.191	6246.3	0.636942	1.209272

(Continued)

TABLE XX (Continued)

VAPOR PRESSURE AND HEATS OF SUBLIMATION OF CARBON DIOXIDE

Temperature, T (°K)	Pressure, P (mm Hg)	Heat of Sublimation (cal/gm mole)	$(1/T) \times 10^2$ ($°K^{-1}$)	Log P (P in mm Hg)
156	14.238	6250.7	0.641025	1.153462
155	12.500	6255.2	0.645161	1.096897
154	10.954	6259.6	0.649350	1.039563
153	9.582	6263.9	0.653594	0.981443
152	8.366	6268.2	0.657894	0.922522
151	7.291	6272.5	0.662251	0.862784
150	6.342	6276.8	0.666666	0.802212
149	5.505	6281.0	0.671140	0.740789
148	4.770	6285.1	0.675675	0.678498
147	4.124	6289.3	0.680272	0.615320
146	3.558	6293.4	0.684931	0.551237
145	3.064	6297.5	0.689655	0.486232
144	2.632	6301.5	0.694444	0.420282
143	2.256	6305.5	0.699300	0.353370
142	1.930	6309.5	0.704225	0.285473
141	1.647	6313.4	0.709219	0.216573
140	1.402	6317.3	0.714285	0.146645
139	1.190	6321.2	0.719424	0.075669
138	1.008	6325.1	0.724637	0.003623
137	8.521 (-1)[a]	6328.9	0.729927	-0.069519
136	7.182 (-1)	6332.7	0.735294	-0.143780

(Continued)

TABLE XX (Continued)

VAPOR PRESSURE AND HEATS OF SUBLIMATION OF CARBON DIOXIDE

Temperature, T (°K)	Pressure, P (mm Hg)	Heat of Sublimation (cal/gm mole)	$(1/T) \times 10^2$ ($°K^{-1}$)	Log P (P in mm Hg)
135	6.037 (-1)	6336.4	0.740740	-0.219186
134	5.061 (-1)	6340.1	0.746268	-0.295761
133	4.231 (-1)	6343.8	0.751879	-0.373533
132	3.528 (-1)	6347.5	0.757575	-0.452529
131	2.932 (-1)	6351.1	0.763358	-0.532775
130	2.431 (-1)	6354.7	0.769230	-0.614303
129	2.008 (-1)	6358.3	0.775193	-0.697141
128	1.655 (-1)	6361.8	0.781250	-0.781320
127	1.359 (-1)	6365.3	0.787401	-0.866871
126	1.112 (-1)	6368.8	0.793650	-0.953828
125	9.074 (-2)	6372.3	0.800000	-1.042224
124	7.377 (-2)	6375.7	0.806451	-1.132093
123	5.978 (-2)	6379.0	0.813008	-1.223477
122	4.826 (-2)	6382.4	0.819672	-1.316402
121	3.882 (-2)	6385.7	0.826446	-1.410913
120	3.111 (-2)	6389.0	0.833333	-1.507048
119	2.484 (-2)	6392.2	0.840336	-1.604849
118	1.975 (-2)	6395.4	0.847457	-1.704358
117	1.565 (-2)	6398.6	0.854700	-1.805619
116	1.234 (-2)	6401.8	0.862068	-1.908676
115	9.692 (-3)	6404.9	0.869565	-2.013577

(Continued)

TABLE XX (Continued)

VAPOR PRESSURE AND HEATS OF SUBLIMATION OF CARBON DIOXIDE

Temperature, T (°K)	Pressure, P (mm Hg)	Heat of Sublimation (cal/gm mole)	$(1/T) \times 10^2$ ($°K^{-1}$)	Log P (P in mm Hg)
114	7.579 (-3)	6408.0	0.877192	-2.120370
113	5.901 (-3)	6411.0	0.884955	-2.229104
112	4.573 (-3)	6414.0	0.892857	-2.339834
111	3.527 (-3)	6417.0	0.900900	-2.452611
110	2.707 (-3)	6419.9	0.909090	-2.567491
109	2.068 (-3)	6422.8	0.917431	-2.684533
108	1.571 (-3)	6425.7	0.925925	-2.803795
107	1.188 (-3)	6428.5	0.934579	-2.925340
106	8.928 (-4)	6431.3	0.943396	-3.049233
105	6.675 (-4)	6434.1	0.952380	-3.175540
104	4.962 (-4)	6436.8	0.961538	-3.304330
103	3.667 (-4)	6439.5	0.970873	-3.435677
102	2.694 (-4)	6442.1	0.980392	-3.569655
101	1.966 (-4)	6444.7	0.990099	-3.706341
100	1.426 (-4)	6447.3	1.00000	-3.845817
99	1.028 (-4)	6449.8	1.01010	-3.988166
98	7.354 (-5)	6452.3	1.02040	-4.133478
97	5.226 (-5)	6454.7	1.03092	-4.281841
96	3.687 (-5)	6457.1	1.04166	-4.433352
95	2.582 (-5)	6459.5	1.05263	-4.588110
94	1.794 (-5)	6461.8	1.06382	-4.746217

(Continued)

TABLE XX (Continued)

VAPOR PRESSURE AND HEATS OF SUBLIMATION OF CARBON DIOXIDE

Temperature, T (°K)	Pressure, P (mm Hg)	Heat of Sublimation (cal/gm mole)	$(1/T) \times 10^2$ (°K-1)	Log P (P in mm Hg)
93	1.237 (-5)	6464.0	1.07526	-4.907782
92	8.454 (-6)	6466.3	1.08695	-5.072916
91	5.731 (-6)	6468.4	1.09890	-5.241738
90	3.852 (-6)	6470.6	1.11111	-5.414369
89	2.565 (-6)	6472.7	1.12359	-5.590936
88	1.692 (-6)	6474.7	1.13636	-5.771575
87	1.106 (-6)	6476.7	1.14942	-5.956423
86	7.151 (-7)	6478.7	1.16279	-6.145629
85	4.578 (-7)	6480.6	1.17647	-6.339343
84	2.899 (-7)	6482.5	1.19047	-6.537729
83	1.816 (-7)	6484.3	1.20481	-6.740952
82	1.124 (-7)	6486.0	1.21951	-6.949188
81	6.876 (-8)	6487.7	1.23457	-7.162669
80	4.155 (-8)	6489.4	1.25000	-7.381453
79	2.478 (-8)	6491.0	1.26582	-7.605878
78	1.458 (-8)	6492.6	1.28205	-7.836113
77	8.465 (-9)	6494.0	1.29870	-8.072385
76	4.843 (-9)	6495.5	1.31578	-8.314928
75	2.729 (-9)	6496.9	1.33333	-8.563993
74	1.514 (-9)	6498.2	1.35135	-8.819842
73	8.265 (-10)	6499.4	1.36986	-9.082754

(Continued)

TABLE XX (Continued)

VAPOR PRESSURE AND HEATS OF SUBLIMATION OF CARBON DIOXIDE

Temperature, T (°K)	Pressure, P (mm Hg)	Heat of Sublimation (cal/gm mole)	$(1/T) \times 10^2$ ($°K^{-1}$)	Log P (P in mm Hg)
72	4.436 (-10)	6500.6	1.38888	-9.353018
71	2.339 (-10)	6501.7	1.40845	-9.630945
70	1.211 (-10)	6502.8	1.42857	-9.916860
69	6.150 (-11)	6503.8	1.44927	-10.211109
68	3.062 (-11)	6504.7	1.47058	-10.514056
67	1.492 (-11)	6505.5	1.49253	-10.826089
66	7.118 (-12)	6506.3	1.51515	-11.147617
65	3.318 (-12)	6507.0	1.53846	-11.479076
64	1.510 (-12)	6507.6	1.56250	-11.820925
63	6.704 (-13)	6508.1	1.58730	-12.173657
62	2.899 (-13)	6508.5	1.61290	-12.537794
61	1.219 (-13)	6508.9	1.63934	-12.913892
60	4.983 (-14)	6509.1	1.66666	-13.302546
59	1.975 (-14)	6509.3	1.69491	-13.704387
58	7.584 (-15)	6509.3	1.72413	-14.120092
57	2.816 (-15)	6509.3	1.75438	-14.550384
56	1.009 (-15)	6509.2	1.78571	-14.996038
55	3.484 (-16)	6509.0	1.81818	-15.457887
54	1.157 (-16)	6508.6	1.85185	-15.936817
53	3.683 (-17)	6508.2	1.88679	-16.433792
52	1.122 (-17)	6507.6	1.92307	-16.949839

(Continued)

TABLE XX (Continued)

VAPOR PRESSURE AND HEATS OF SUBLIMATION OF CARBON DIOXIDE

Temperature, T (°K)	Pressure, P (mm Hg)	Heat of Sublimation (cal/gm mole)	$(1/T) \times 10^2$ ($°K^{-1}$)	Log P (P in mm Hg)
51	3.265 (-18)	6506.9	1.96078	-17.486074
50	9.043 (-19)	6506.1	2.00000	-18.043695
49	2.377 (-19)	6505.2	2.04081	-18.623998
48	5.910 (-20)	6504.2	2.08333	-19.228390
47	1.386 (-20)	6503.0	2.12765	-19.858391
46	3.050 (-21)	6501.7	2.17391	-20.515660
45	6.281 (-22)	6500.2	2.22222	-21.201995
44	1.204 (-22)	6498.6	2.27272	-21.919359
43	2.138 (-23)	6496.9	2.32558	-22.669899
42	3.500 (-24)	6495.0	2.38095	-23.455959
41	5.247 (-25)	6493.0	2.43902	-24.280117
40	7.158 (-26)	6490.8	2.50000	-25.145203

[a]Numbers in parentheses indicate powers of 10 by which pressure entry is to be multiplied; thus 8.521 (-1) = 0.8521.

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

October 22, 1963

FINAL REPORT

TO: Mr. B. W. Birmingham, Scientific Officer

FROM: W. T. Ziegler, Project Director

SUBJECT: Final Report on Contract No. CST-7404 (Our Project No. A-663) for the Period December 1, 1962 through August 31, 1963.

Work Originally Proposed

The work to be carried out under this contract involved the calculation of the vapor pressure and heats of vaporization and sublimation of the following substances:

a) Nitrogen and fluorine;
b) Carbon dioxide, carbon monoxide;
c) Krypton, xenon;
d) Acetylene, ethane and propane.

These substances were to be investigated approximately in the order given. The original proposal on which this contract was based indicated that calculations for nitrogen, fluorine, carbon monoxide and carbon dioxide could probably be completed with the time and funds requested, with some work being carried out on certain of the other gases. During the period of the contract, telephone conversations with Mr. B. W. Birmingham and Mr. V. J. Johnson of the Cryogenic Engineering Laboratory indicated the desirability of making similar calculations for normal hydrogen (75 per cent orthohydrogen and 25 per cent parahydrogen.)

Work Completed

Calculations of the vapor pressure and heats of vaporization and sublimation were completed for the substances listed below from the temperature corresponding to a vapor pressure of one atmosphere to a temperature at which the vapor pressure was very low:

	Range		
Nitrogen	77.35° K (1 atm)	to	10° K (P = 1.06×10^{-30} torr)
Fluorine	85.03° K (1 atm)	to	14° K (P = 7.86×10^{-25} torr)
Carbon Monoxide	81.64° K (1 atm)	to	14° K (P = 1.47×10^{-23} torr)
Carbon Dioxide	194.69° K (1 atm)	to	40° K (P = 7.1×10^{-26} torr)

The results have been presented in the following reports. Twenty copies of each report have been supplied to the Contracting Officer. Three hundred copies of each report were supplied under separate purchase orders to the Cryogenic Data Center, National Bureau of Standards (Attn. Mr. V. J. Johnson).

"Calculation of the Vapor Pressure and Heats of Vaporization and Sublimation of Liquids and Solids, Especially Below One Atmosphere Pressure. IV. Nitrogen and Fluorine," W. T. Ziegler and J. C. Mullins. Tech. Rpt. No. 1, Project A-663, Engineering Experiment Station, Georgia Institute of Technology, April 15, 1963 (Contract No. CST-7404, National Bureau of Standards, Boulder, Colorado.)

"Calculation of the Vapor Pressure and Heats of Vaporization and Sublimation of Liquids and Solids, Especially Below One Atmosphere Pressure. V. Carbon Monoxide and Carbon Dioxide," J. C. Mullins, B. S. Kirk and W. T. Ziegler, Tech. Rpt. No. 2, Project A-663, Engineering Experiment Station, Georgia Institute of Technology, August 15, 1963. (Contract No. CST-7404, National Bureau of Standards, Boulder, Colorado.)

A small computational error was discovered in certain calculations presented in Technical Report No. 1 for nitrogen and fluorine. Correction sheets pointing out these errors were issued on July 2, 1963. Correction sheets pointing out a similar error in the results for argon (Tech. Report No. 2, NBS Contract No. CST-7238) were also issued. The errors are quite small and do not affect the conclusions reached in the subject reports.

Work Partly Completed

Considerable work was done on both krypton and normal hydrogen but no final results were obtained since both time and funds were exhausted before they could be completed. No work was done on the other substances listed above.

Proposed Additional Work

A proposal requesting additional funds to permit completion of the calculations (vapor pressure and heats of vaporization and sublimation) for krypton and

hydrogen, and for carrying out similar calculations for acetylene and ethane has been sent to Mr. V. J. Johnson, Cryogenic Engineering Laboratory, National Bureau of Standards, Boulder, Colorado, for technical review. It is hoped that these additional funds will be granted.

Respectfully submitted,

W. T. Ziegler
Project Director

Approved:

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